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REVIEW OF IGNITION AND FLAMMABILITY PROPERTIES OF LUBRICANTS

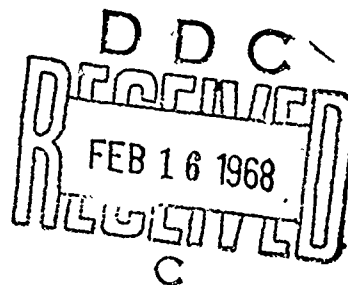
Joseph M. Kuchta
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Bureau of Mines

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Air Force Aero Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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FOREWORD

This report was prepared by the Explosives Research Center of the U.S. Bureau of Mines under USAF Contract No. DO 33(615)-66-5005. The contract was initiated under Project No. 3048 "Fuels, Lubrication and Hazards", Task No. 304807 "Aerospace Vehicle Hazard Protection". It was administered under the direction of the Air Force Aero Propulsion Laboratory, Research and Technology Division, with Mr. Benito P. Botteri as project engineer.

The information presented in this report was requested by the members of the Coordinating Research Council (Aviation Explosive Limits Panel of the Group on Gas Turbine Lubrication) at their annual meeting held at the U.S. Bureau of Mines Explosives Research Center, Pittsburgh, Pa. on September 28, 1966.

This report is based partly on information which was obtained by the Bureau of Mines under the present Air Force Contract DO 33(615)-66-5005 during the period 1 January 1966 to 31 July 1967. Dr. Robert W. Van Dolah was the administrator for the U.S. Bureau of Mines and Messrs. J. M. Kuchta, R. J. Cato, I. Spolan, W. H. Gilbert, and Miss A. C. Imhof actively participated in this work at the U.S. Bureau of Mines Explosives Research Center, Bruceton, Pa. Information is also included from preceding Air Force contracts as follows:

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This technical report has been reviewed and is approved.

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ABSTRACT

The ignition temperature and flammability properties of combustible fluids are useful in determining safety guidelines and in assessing the fire or explosion hazard which may exist in the environment where the fluids are employed. This report is a compilation and review of such information for over 90 lubricants and hydraulic fluids. Particular emphasis is given to those fluids used in aircraft applications. Data are presented for petroleum base fluids and purely synthetic fluids in air, oxygen, and oxygen-nitrogen atmospheres at pressures from 1/8 to 1000 atmospheres. The temperature requirements for ignitions in heated vessels, by heated wires, and by jets of hot gas are compared over a range of heat source dimensions. Similarly, the flash points, flammability limits, decomposition temperatures, and other related properties are compared and discussed for the various classes of lubricants.

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INTRODUCTION

Most lubricants are hydrocarbon-base fluids which can form flammable mixtures with air or other oxidants at certain temperature and pressure conditions. The formation of flammable mixtures in a heated chamber or pipe can be hazardous since autoignition may result from contact of the flammable mixture with a heated surface, such as the heated walls of the chamber. Ignition may also result from exposure of the mixture to a jet of hot gas, an electrical spark, and other energy sources. Thus, the ignition temperature and flammability characteristics of lubricating fluids are useful in assessing the fire or explosion hazard which may arise during their use and storage. Although such information has been obtained for various lubricating materials by the Bureau of Mines (Refs 1-10) and other investigators (Refs 11-24), the data are scattered throughout a number of reports; also, some of the reports have had little distribution. Therefore, the present report was prepared to compare and review the data available for a number of aircraft lubricants, engine oils, and hydraulic fluids. Most of the ignition and flammability data presented here are from Bureau investigations conducted for the Air Force and the producers of lubricants.

A major portion of this report is devoted to the minimum autoignition temperatures (AIT's) of the combustible fluids in heated vessels. Data are presented for petroleum-base lubricants and purely synthetic lubricants in air, oxygen, and various oxygen-nitrogen atmospheres at pressures as low as 1/8 atmosphere and as high as 1000 atmospheres. Unless specified otherwise, the minimum AIT values refer to autoignitions that were evidenced by the appearance of flame. The Bureau values which are reported were obtained in reaction vessels of at least the capacity (200 cc) recommended in the latest ASTM test method (Ref 49); however, some of the results of other investigators that are cited were found in smaller vessels. In the use of these data, it must be recognized that AIT's tend to be lower in the larger reaction vessels and where pressure rise or temperature rise, instead of visible flame, is taken as the ignition criterion. In this connection, data are included for the combustible materials on the variation of their AIT's with vessel size, vessel material, heating time or ignition delay, injection pressure, and ignition criterion. Static and dynamic conditions are considered.

The ignition temperatures obtained in heated vessels are also compared to those found with heated wires or rods and with jets of hot air. In addition, data available on the flash points, flammability limits, decomposition temperatures, and other related properties are presented and discussed. Although data are not given for all available lubricants, the authors have attempted to include information on most of the different chemical classes which comprise such fluids. Information that is particularly lacking for the lubricants is that related to the potential hazards of spontaneous heating, that is, ignition by slow oxidation at low initial environmental temperatures.

PHYSICAL AND STABILITY PROPERTIES OF LUBRICANTS

The two principal classes of lubricants that are used today for military and industrial applications are the synthetics and the petroleum-base materials. In general, the physical and stability properties of a lubricant give a fairly good indication of its possible applications and limitations. When possible, the synthetic lubricants are formulated to provide fluid properties which are compatible with their desired applications. For example, a synthetic lubricant that is being considered as an advanced candidate hydraulic fluid must have good thermal stability but not necessarily high oxidative stability, since it is not designed for use in an oxidizing atmosphere. In contrast, a candidate aircraft engine oil must show resistance to both thermal and oxidative degradation. In addition, the candidate fluid should have low volatility and good lubricity along with a number of other desirable fluid characteristics. The general fluid properties of various classes of lubricants and the requirements for different applications have been discussed in a number of survey papers, including those by Moreton (Ref 25), Dukek (Ref 26), and Adamczak, Benzing, and Schwenker (Ref 27).

Several classes of synthetic lubricants have received considerable attention in recent years because of claims that they are either highly fire resistant or have excellent oxidation resistance, even at elevated temperatures. The phosphate ester, polyphenyl ether, and halogenated hydrocarbon materials are three chemical classes of synthetic lubricants which are claimed to have such properties. Some other specific classes are the dibasic acid esters, silicones, silicate esters, and polyglycol ether compounds, which as a whole tend to have lower oxidative stability or fire resistance than the three classes mentioned above. A qualitative comparison of the thermal and oxidative stability and other fluid properties reported for these lubricant classes is given in Table 1 (Ref 25); similar information for an average mineral oil is also included.

Some of the petroleum base lubricants have fluid properties nearly comparable to those reported for the most highly rated synthetic lubricants. Highly refined paraffinic and naphthenic-base stock mineral oils are two types of petroleum lubricants with relatively good fluid properties over a rather wide temperature range. However, the fire resistance of this class of fluids as a whole is relatively poor compared to the other classes mentioned here. The fire resistance of the water-glycol fluids also is superior to the mineral oils.

The minimum temperature at which a lubricant decomposes in an inert atmosphere is frequently used in comparing thermal stabilities. Table 2 lists such values and other physical properties for various classes of lubricants. Also listed are flash point and autoignition temperature data which are used in rating the potential fire hazard associated with the fluids; these are discussed in other sections of this report.

TABLE 1. General Properties of Some Classes of Synthetic Lubricants and Refined Mineral Oil.^{1/}

Class	Volatility	Viscosity					Fire Resistance
		Temperature Character-istics	Oxidation Resistance	Lubricity	Thermal Stability	Hydrolysis Resistance	
Dibasic Acid Esters	Generally lower than petroleum oils	G to E	F to G	F to G	F to G	F to G	P to F
Phosphate Esters	Generally lower than petroleum oils	F to G	G to E	G to E	P to F	P to G	G to E
Silicones	Much lower than petroleum oils	E	E	P to F	F to E	E	P to G
Silicate Esters	Lower than petroleum oils	E	P to F	F	E	P to F	P to F
Polyglycol ether compounds	Approximately equal, some lower than petroleum oils	G to E	P to F	G	F to G	F to G	F to G
Trifluoro vinyl chloride polymers	Some lower, some higher than petroleum oils	VP	E	P to E	E	E	E
Average mineral oil (well refined)	--	F to G	F to G	F to G	F to G	E	P

The following code is used to indicate the range of each property described herein.

E for Excellent G for Good F for Fair P for Poor VP for Very Poor

^{1/} Information from Ref. 25.

TABLE 2. - Physical and Other Properties of Lubricating Oils, Engine Oils, and Hydraulic Fluids.^{1/}

Fluid	Chemical Class or Compound	Viscosity, cs		Specific Gravity (Water=1)	Flash Point °F	Fire Point °F	Autoignition ^{2/} Temperature °F	Decomposition Temperature °F
		100°F	210°F					
<u>Mineral Oils</u>								
MIL-2190	Mineral Oil	32.2	5.8	0.86	~450	--	665(5)	--
Harmony 44 (Gulf)	"	87.6	9.8	0.83	~460	--	680(5)	--
MLO-5731	" - Naphthenic	--	--	--	--	--	--	640(28)
MLO-7277	"	--	--	--	--	--	464(50)	725(30)
MLO-60-294	" - Paraffinic, deep Dewaxed	14	3.15	0.88	385	430	700(27)	~620(30)
Mobil DTE-103	Mineral Oil	124	8.74 to 10.2	0.92	390	--	702, 675(50)	--
MIL-H-6083B	"	--	--	--	255	--	470(50)	--
MIL-H-5606A	"	--	--	--	--	--	437(4)	--
MIL-O-5606(Esso Univilis J-43)	"	--	--	--	195	225	437(2)	--
<u>Glycols and Water Glycols</u>								
Ethylene Glycol	Glycol	8.7	--	--	240	--	856(38)	--
Propylene Glycol	"	19.6	--	--	230	235	835(38)	--
Ethylene Glycol + 50% Water	Water-Glycol	2.2	--	--	--	--	903(38)	--
Houghto-Safe 271	"	~43	--	1.045	--	--	767(5)	--
" " 520	"	43.2	~16(150°F)	1.075	--	--	--	--
" " 620	"	43.2	25.1(130°F)	1.055	--	--	--	--
Nyvac 20(Mobil)	"	41	29.8(150°F)	1.07	--	--	750(51)	--
Irus 902 (Shell)	Water-Glycol and additives	97.4	51	0.93	--	--	769(51)	--
Ucon 50HB-260	Water-Oil Emulsion	56	--	--	455	500	743(38)	--
Ucon 50HB-280-X	Polyalkylene Glycol	--	--	--	500	600	743(20)	--
Ucon LB-60	"	10.7	--	--	310	325	653(38)	--
Ucon LB-400-X	"	--	--	--	--	--	752(20)	--
<u>Phosphate Esters</u>								
Houghto-Safe 1010	Triaryl Phosphate Ester	18.2	3.9	1.20	505	670	>1200(51)	--
" " 1055	"	13.0	8.0	1.145	505	680	1020, 830(50)	--
" " 1115	"	32.2	4.1	1.165	--	680	>1200(51)	--
" " 1120	"	49.8	5.0	1.15	485	690	1020(5)	--
" " 1130	"	62.8	6.0	1.145	490	680	>1200(51)	--

Table 2 (Cont)

Fluid	Chemical Class or Compound	Viscosity, cs		Specific Gravity (Water=1)	Flash Point °F	Fire Point °F	Autoignition ² Temperature °F	Decomposition Temperature °F
		100°F	210°F					
Phosphate Esters (Cont)								
MIL-H-19457 (Type 1)	Triaryl Phosphate Ester	--	--	--	--	--	1040(19)	--
Tricresyl Phosphate	"	38.3	4.48	1.17	470	--	1110(12)	680(48)
Trioctyl Phosphate	Trialkyl Phosphate Ester	--	--	0.926	405	--	545(13)	~380(28)
Trihexyl Phosphate	"	--	--	--	--	--	549(12)	--
Pydraul AC	Phosphate Ester-Chlorinated Hydrocarbon	88.8	5.0	1.36	450	745	1148(5)	--
Pydraul F-9	"	50.9	5.9	1.285	430	675	1100(51)	--
Cellulube 220 (Shell S.F.R.)	Phosphate Ester	43.4	4.9	1.145	455	665	1038(5)	--
Pydraul 150 (Monsanto)	"	30.5	7.9	1.125	380	470	975(51)	--
Skydrol	"	--	--	--	360	470	>1300(51)	--
Mono- and Dibasic Acid Esters								
Plexol 201	Di-2-hexyl Sebacate	12.7	3.31	0.912	420	450	--	--
Plexol 244	Di-isooctyl Adipate	9.64	2.77	0.926	400	445	712(12)	--
Plexol 273	Di-isodecyl Adipate	14.5	3.56	0.920	425	460	--	--
Plexol 79	Polyester	1,250	108	1.023	540	620	--	--
MIL-L-7808 (O-60-18, Esso 4040)	Sebacate-adipate Diester	12.1	3.1	--	437	460	--	--
MIL-L-7808 (H-1026)	"	12.58	3.3	--	430	475	728, 436(7)	490(26)
MIL-L-9236B (O-60-7, TP-653B)	Di-2-ethylhexyl Sebacate	15.1	3.4	--	435	485	755(50)	575(15)
MIL-L-9236 (O-60-27)	Trimethylol Propane Ester	14.8	3.45	--	470	525	738, 491(7)	~650(24)
MIL-L-9236 (O-60-23)	"	15.99	3.62	--	490	535	--	--
MIL-L-9236 (O-61-17)	"	15.78	3.59	--	425	510	--	--
MIL-L-9236B	"	16	3.2	0.97	435	475	--	--
MLO-54-581 (Texaco, TL-2456)	Diester	--	--	--	425	510	>800(51)	~650(24)
TP 653B (Hey Newport)	Trimethylol Propane Ester	--	--	~0.97	435	475	734(2)	--
P/O (Esso 4275)	Polyester	--	8.04	0.951	510	--	705, 507(50)	--
MLO-60-50	Trimethylol Propane Ester	--	--	--	--	--	711, 500(50)	--
Trimethylolpropane Tri-pelargonate	"	--	--	--	--	--	--	748(30)
	"	--	--	--	--	--	--	606(26)
Silanes								
MLO-54-408C	Tetra Dodecyl Silane	34.58	6.37	--	555	625	775(17)	658(15)
MLO-56-280	Diphenyl di-n-dodecyl Silane	37.2	6.2	--	530	580	690(17)	>680(15)
MLO-56-578	Octadecyl trioctyl Silane	27.5	5.76	--	520	590	790(17)	--

Table 2 (Cont)

Fluid	Chemical Class or Compound	Viscosity, cs		Specific Gravity (Water=1)	Flash Point °F	Fire Point °F	Autoignition Temperature °F	Decomposition Temperature °F
		100°F	210°F					
Silanes (Cont.)								
MLO-56-582	Octadecyl tridecyl Silane	33.9	6.8	--	545	595	750(17)	--
MLO-56-610	Dodecyl tridecyl Silane	26.4	5.6	--	535	575	750(17)	--
MLO-56-611	Didodecyl dioctyl Silane	23.1	5.0	--	520	565	750(17)	--
MLO-57-9	Tetra undecyl Silane	29.26	6.11	--	545	600	760(17)	--
Silicates and Silicones								
Tetra (2-ethylhexyl)Silicate	Ethyl hexyl Silicate	--	--	--	--	--	--	638(28)
Orsil B.F.1	(2-ethylhexyl) Silicate	--	--	--	--	--	~570(12)	--
Oronite 8200	Silicate Ester	31.75	11.14	--	385	440	716(2)	--
Oronite 8515	"	24.3	8.11	--	390	450	713(50)	--
MLO-54-645	85% Oronite & 15% Plexol	--	--	--	340	455	716(2)	--
MLO-54-540 (Monsanto OS-45)	Silicate Ester	--	--	--	325	430	703(2)	--
MLO-54-856 (Hillingshead, 72073C)	"	--	--	--	315	440	716(2)	--
Versilube F-50	Silicone	52	16	1.045	550	640	900(51)	>600(51)
Versilube F-44	"	55	17	1.045	550	640	900(51)	>600(51)
Dow Corning 190	Polymethyl Siloxane	22.6	--	--	240	--	860(38)	--
Dow Corning 400	Polymethyl Siloxane	10.9	--	--	255	280	610(38)	--
Dow Corning 500	Polyethyl Siloxane	44.9	--	--	470	--	900(38)	--
Dow Corning 550	Silicone	65 to 87	--	1.065	600	--	--	740(28)
Dow Corning 700	Poly (methyl, phenyl) Siloxane	2.8	--	--	305	325	940(38)	--
Dow Corning 710	Methyl Phenyl Silicone	220	--	1.112	520	--	--	588(15)
MLO-59-98	50% Methyl Phenyl Silicone (DC 258) plus 50% TBP Adipate Tetracoproate	61.8	13.5	--	--	--	--	625(30)
Halogenated Silicones and Hydrocarbons								
MLO-53-446 (GE 81406)	Chlorinated Silicone	--	--	--	580	710	786(2)	514(15)
MLO-59-287 (GE F-50)	Chlorophenyl Methyl Silicone	--	--	--	--	--	--	630(30)
Fluorolube F-S	Polytrifluorochloroethylene	5	--	1.86	--	--	~1205(12)	>620(51)
Pydraul A-200	Chlorinated Hydrocarbon	49.8	5.0	1.42	350	680	1200(51)	--
Arochlor-1248	Tetrachlorodiphenyl	43.0	3.2	1.41	380	None	~1185(12)	--
Arochlor-1242	Trichlorodiphenyl	17.7	--	--	350	633	1230(38)	--
Arochlor-1254	Chlorinated Hydrocarbon	--	--	--	--	--	~1085(12)	--

Table 2 (Cont)

Fluid	Chemical Class or Compound	Viscosity, cs		Specific Gravity (Water=1)	Flash Point °F	Fire Point °F	Autoignition ^{1/} Temperature °F	Decomposition Temperature °F
		100°F	210°F					
<u>Aromatic Ethers</u>								
OS-124 (Monsanto, 5P4E)	5 Ring Polyphenyl Ether	363	13.1	1.20	550	660	1112(50)	≥830(30)
MCS-293 (Monsanto)	Aromatic Ether	25.2	4.13	1.19	428	518	914(50)	675
MLO-59-692 (Monsanto)	Bis (phenoxyphenoxy) Benzene	--	--	--	--	--	--	942(30)
mm-4P4E	Bis(m-phenoxyphenyl) Ether	60.9	5.98	--	465	--	1095(17)	~835(17)
pp-4P3E	Bis(p-phenoxyphenyl) Ether	2.83(300°F)	1.51(400°F)	--	516	585	1040(17)	~835(15)
mm-5P4E	m-Bis(m-phenoxyphenoxy) Benzene	332	12.7	--	540	660	1050(17)	870(17)
5P4E	Bis(phenoxyphenoxy) Benzene	380	13.4	--	560	660	1130, 1030(7)	870(26)
pppp-6P5E	Bis [p-(p-phenoxyphenoxy)phenyl] Ether	4.20(400°F)	1.55(600°F)	--	635	--	1030(17)	773(15)
<u>Phosphonitriles</u>								
MLO-63-24	Hexaphenyltriphosphonitrile	--	--	--	--	--	--	810(30)
MLO-63-25	Phenoxy base Triphosphonitrile	--	--	--	--	--	--	905(30)
K488 (Olin Matheson)	Tetrameric Octylfluoroamyl Phosphonitrilate	--	--	--	--	--	900(19)	--
<u>Miscellaneous Oils</u>								
Lard oil		--	--	<1	395	--	833(47)	--
Linseed oil		--	--	0.95	435	535	820(47)	--
Lube oil, cylinder		--	--	<1	--	535	783(47)	--
" " , light machine		--	--	<1	318	370	--	--
" " , spindie		--	--	<1	169	200	--	--
Menhaden oil		--	--	0.927	435	--	828(47)	--
Mineral seal oil		--	--	--	170	255	--	--
Olive oil		--	--	0.91	437	--	826(47)	--
Palm oil		--	--	0.92	421	--	650(47)	--
Pine oil		--	--	0.86	172	175	--	--
Rapeseed oil		--	--	0.915	325	550	836(47)	--
Rosin oil		--	--	0.98-1.1	266	--	648(47)	--
Soybean oil		--	--	0.925	540	--	833(47)	--
Tung oil		--	--	0.94	552	--	855(47)	--
Turkey-red oil		--	--	--	476	--	833(47)	--
S.A.E. No. 10 lube oil		--	--	--	340	380	720(20)	--
S.A.E. No. 60 lube oil		--	--	--	480	620	770(20)	--

^{1/} Autoignition and decomposition temperature data from references cited in parentheses. Viscosity, specific gravity, flash point, and fire point data mainly from vendor's literature.

^{2/} Ignition evidenced by visible flame except for underlined values where sudden pressure rise was used. Bureau of Mines data (Refs 2, 4, 5, 7, and 50) were obtained using reaction vessels ≥200 cc. Values listed for other references were determined in reaction vessels ≤125 cc.

Since decomposition temperatures can vary greatly with chemical structure, it is almost useless to compare these values when the lubricant class is grossly specified. Blake, et al (Ref 28) have published an excellent analysis on the effect of chemical structure on the thermal stability of over 100 organic compounds; similar noteworthy studies have been made by Brown (Ref 39), Krawetz (Ref 30), Mahoney (Refs 15-16), Bolt (Ref 18), Martynov (Ref 31), and their coworkers for various lubricating materials. Table 3 shows the approximate order of thermal stability that appears to exist for the specified classes of lubricants, according to the available data.

TABLE 3. Approximate Order of Thermal Stability for Various Classes of Lubricants Based on Decomposition Temperatures.

<u>Decomp Temp Range</u>	<u>Lubricant Class</u>
700°-900°F	Aromatic or Polyphenyl Ethers
	Aromatic Phosphate Esters
	Aromatic Silicates, Silanes, and Silicones
600°-700°F	Aliphatic Silicates, Silanes, and Silicones
	Mineral Oils - Naphthenic
	Mineral Oils - Paraffinic
	Halogenated Hydrocarbon Esters
	Polyol Hydrocarbon Esters
400°-600°F	Sebacate Esters
	Aliphatic Phosphate Esters

Although some overlapping can be expected for the various lubricant classes, the indicated order of stability is useful in explaining the ignition behavior of the lubricant classes at temperatures above those required for their decomposition. It is worth noting that the fluids containing aromatic groups tend to be more thermally stable than those with aliphatic groups. The fluids with aromatic groups also have greater oxidative stability as confirmed by the AIT data presented here.

LIMITS OF FLAMMABILITY

The lower and upper limits of flammability of a combustible-oxidant system are of interest since they delineate the range of mixture compositions over which flame propagation will occur when the mixture is ignited. The general flammability diagram shown in Figure 1 illustrates the effect of temperature on the limits of flammability of a combustible vapor in air at a constant initial pressure. The region to the left of the saturated vapor-air mixture curve labeled "mist" represents the zone where flammable

mists or sprays and vapor-air mixtures can coexist. All the mixtures to the right of the saturated vapor-air mixture curve and between the lower and upper limit-of-flammability curves are flammable vapor-air mixtures. If these mixtures are ignited by an external energy source, such as an electrical spark, they can be expected to propagate flame. Furthermore, if these same mixtures are heated sufficiently, as in a heated vessel, they can ignite without an external energy source; the minimum temperature required is labeled "AIT" in Figure 1. A review of ignition and flammability concepts that are pertinent to this discussion has been made by Van Dolah, et al. (Ref 40).

In practice, the lower (lean) limit of flammability is of greatest interest since it defines the minimum vapor concentration of a given combustible required for flame propagation in a specified oxidant atmosphere. The minimum temperature at which a lower limit concentration can exist depends upon the volatility of the combustible and corresponds approximately to its flash point (T_L in Figure 1); Table 2 lists the flash points of the various lubricants discussed in this report. The maximum combustible vapor concentration which can propagate flame in an oxidant atmosphere is the upper limit of flammability. Generally, the lower limit of flammability decreases only slightly with moderate increases in temperature, pressure, and oxygen concentration, whereas the upper limit increases and is usually affected more by such changes in conditions. It is also of interest to note that flash points of combustible liquids increase with increased pressure.

Table 4 lists the lower and upper limits of flammability obtained at this laboratory for two hydraulic fluids (MIL-H-6083B and Oronite 8515) and two aircraft engine oils (MIL-L-7808 and H-1026); flash point data are also included. Here, the limits are reported in weight percent and weight of combustible per liter of air at S.T.P. conditions (32°F and 1 atm). As noted, the lower limits for these combustibles did not vary greatly, although the flash point of the MIL-H-6083B mineral oil (225°F) was much lower than those ($\geq 390^\circ\text{F}$) of the sebacate ester oils (MIL-L-7808 and H-1026) and the silicate ester fluid (Oronite 8515). The lower limits varied from 3.3 to 5.0 weight percent or 45 to 64 mg/liter. Zabetakis (Ref 1) has shown that the lower limit values for many hydrocarbon combustibles having molecular weights between 58 and 230 are all approximately 45 mg/liter. In comparison, the upper limits for the engine oils were between 14.5 and 15.0 weight percent (226 to 238 mg/liter) and much lower than the value of 31.8 percent (601 mg/liter) for the MIL-H-6083B mineral oil. Thus, the range of flammability is greater with the latter fluid.

TABLE 4. Flammability Limits and Flash Points of Two Hydraulic Fluids and Two Engine Oils in Air at Atmospheric Pressure.

Bureau of Mines F-11 Apparatus - 2-inch diameter tube

Initial Temperature °F	Lower Limit ^{1/}		Upper Limit ^{1/}		Flash Point ^{2/} °F
	Wt.%	mg/liter of air	Wt.%	mg/liter of air	
<u>MIL-H-6083B Hydraulic Fluid (Mineral Oil)</u>					
400	4.6	62	31.8	601	225
<u>Oronite 8515 Hydraulic Fluid (Silicate Ester)</u>					
550	4.7	64	--	--	390
<u>MIL-L-7808 Oil (Sebacate-adipate diester)</u>					
500-550	3.4	45	15.0	238	445
<u>H-1026 Oil (Sebacate Ester)</u>					
550	4.4	60	14.5	226	~450

^{1/} g/liter approximately equal to oz/ft³.

^{2/} Determined in Cleveland Open Cup Tester.

Because of the high molecular weight of most lubricants, their limits are relatively low when expressed on a volume basis. For example, the 64 mg/l for the Oronite fluid is equivalent to approximately 0.2 volume percent. Its lower limit is essentially the same in air and oxygen. A partial flammability diagram for this hydraulic fluid in various oxygen-nitrogen mixtures is shown in Figure 2. This figure indicates that the critical oxygen concentration below which flammable mixtures will not form with this fluid is 9.7 volume percent at a mixture temperature of 550°F; the critical oxygen values for many saturated and unsaturated hydrocarbon fuels are between 11 and 12 percent at near room temperature (Ref 1). As a fair approximation, the lower limits for such hydrocarbon combustibles in air can be calculated from the theoretical fuel concentration required for complete combustion (T.C.C.):

$$\text{Lower limit (Vol \%)} = 0.5 \times \text{T.C.C. (Vol \%)} \quad (1)$$

Burgoyne, Newitt, and Thomas (Ref 32) measured the lower limit of flammability of fine lubricating oil mists in air and obtained a value of 49 mg/liter of air with oil drop sizes ranging between 2 and 20 microns. They also reported comparable values for the lower limits of condensed mists of various commercial oils including several mineral cutting oils (Table 5), and of oil sprays of various droplet sizes; the limits ranged between 40 and 60 mg/liter for these oils (Refs 33 and 34). Similar lower limit values would be expected for the mists or vapor-air mixtures of other petroleum base lubricants. Ordinarily, if the fuel droplets in mists are less than 10 microns in size, the limit data will tend to be comparable to those of the fuel vapor-oxidant mixtures. Also, it should be noted that a lubricant can form such flammable mists or sprays in air at temperatures far below its flash point.

The approximate flash point range of the various classes of lubricants are compared in Table 6. The flash points of some of the lubricant classes, particularly the mineral oils, extend over a greater temperature range ($\sim 200^{\circ}$ to 450°F) than observed for the others. Nevertheless, most of the mineral oils and the silicate esters are capable of forming flammable vapor-air mixtures at lower temperatures than those required for the other lubricant classes. The water-glycols (some of which may not be flammable) and the lubricants having the higher decomposition temperatures tend to have the higher flash points according to the available data; however, it is not implied here that flash points are related to decomposition temperatures.

TABLE 5. Lower Limits of Flammability of Condensed Mists of Commercial Oils in Air at Atmospheric Pressure.^{1/}

	Lower Limit ^{2/} mg/liter of air	Flash Point ^{3/} °F
Mineral cutting oil, No. 1	42	266
Mineral cutting oil, No. 2	56	293
Mineral cutting oil No. 2 after straight distillation	55	230
Mineral cutting oil, No. 3 (Shell M.6)	49	--
Sperm quenching oil	46	--
Pool diesel oil	49	--

^{1/} Data from Refs 33 and 34.

^{2/} Oz/ft³ of air approximately equal to g/liter of air.

^{3/} Closed cup method.

TABLE 6. Approximate Flash Point Range of the Various
Classes of Lubricants.

<u>High Flash Point</u> 500°-700°F	Water - Glycols
	Aromatic Ethers
	Silicones and Chlorinated Silicones
	Aliphatic Silanes
<u>Medium Flash Point</u> 400°-500°F	Aromatic Phosphate Esters
	Polyol Hydrocarbon Esters
	Sebacate and Adipate Esters
	Aliphatic Phosphate Esters
<u>Low Flash Point</u> 200°-400°F	Mineral Oils
	Silicate Esters
	Mineral Oils

Various spray flammability-type tests are used to rate the flammability hazard of lubricants and other similar fluids (Refs 14, 35, 36, 37 and 38). Some of the methods are qualitative and indicate only whether the fluid spray can propagate a flame when the spray is ignited in air with a suitable ignition source, such as a torch. In others, the critical oxygen concentration below which flame propagation does not occur with the spray is measured using various oxygen-nitrogen mixtures. Sullivan, Wolfe and Zisman (Ref 38) obtained such data for a number of aircraft fuels and lubricating fluids as shown in Table 7. Gassmann (Ref 14) rated the flammability hazard of these and several other fluids by measuring the percent of hexachlorobutadiene required to produce a sharp decrease in flame length. As noted in Table 7, the flammability ratings obtained by the two methods are not in agreement. For example, the ratings for the tri-octylphosphate and tricresylphosphate fluids reflect a higher order of flammability hazard by Sullivan's method. The ratings are not necessarily expected to be the same by the two methods, since one indicates the effect of an inert gas (nitrogen), while the other indicates the effect of an inhibitor vapor (hexachlorobutadiene) whose physical and chemical properties are much different from those of nitrogen. Generally, the flammability characteristics of combustible sprays and vapors should be determined in the oxidant-diluent atmospheres which are encountered in practice. Also, the effect of droplet size should be considered since any combustible lubricant capable of forming flammable vapor-air mixtures will form flammable mists or fogs.

TABLE 7. Flammability and Ignition Characteristics of Fluids.^{1/}

Fluid	Supplier	Flash Point °F	Fire Point °F	Spontaneous Ignition Temp. °F _{3/}	Spray Flammability Limit _{3/} % Oxygen	Spray Flammability Rating _{4/}
Aviation gasoline (100 oct.)		123 _{2/}		1295	12	80
366 base stock	Standard Oil Dev. Co.	215 _{2/}	220 _{2/}	500	12	72
Kerosene	The Texas Co.	130 _{2/}				72
Lub oil 2075 (SAE No. 10)	The Texas Co.	340 _{2/}	380 _{2/}			70
Lub oil 1120 (SAE No. 60)	The Texas Co.	480 _{2/}	620 _{2/}			69
Ucon LB-400-X	Carbide & Carbon Chem. Corp.			752	54	65
Ucon 50-HB-280-X	Carbide & Carbon Chem. Corp.	500 _{2/}	600 _{2/}	743	43	64
Triethylphosphate	Standard Oil Dev. Co.	380 _{3/}	465 _{3/}	680	13	61
Skydrol	(Monsanto Chemical Co.)	360 _{2/}	470 _{2/}	>1300 _{2/}	25	55
Tricresylphosphate	(Douglas Aircraft Co.)					
Butyl Tetrachlorophthalate	Monsanto Chemical Co.	500 _{3/}	685 _{3/}	1170	19	48
Santicizer 140	Commercial Solvents Corp.					44
Formulation No. 9	Monsanto Chemical Co.					42
Hexachlorobutadiene	Standard Oil Dev. Co.	None _{2/}	None _{2/}	>1000	77	<30
Hydrolube						0
Hollingshead H-2	Hollingshead Research Div.			885	67	0
RPM Hydraulic fluid	California Research Corp.					0
Perfluorotriethylamine	Minnesota Mining & Mfg. Co.					0
Perfluorodimethylpropylamine	Minnesota Mining & Mfg. Co.					0
Hexachloropropene	Dow Chemical Co.					0

1/ Information from Ref. 14.

2/ Manufacturers' data.

3/ Information from Ref. 38

4/ Percent hexachlorobutadiene added to the fluid spray to produce a sharp decrease in flame length.

AUTOIGNITION TEMPERATURES

1. Effect of Vessel Size and Material

The lowest ignition temperatures of combustible gases and vapors are normally found by injecting the combustible material into a relatively large heated vessel to minimize any wall effects; static conditions (quiescent oxidant atmospheres) are maintained to permit sufficient fuel contact time for ignition to occur. Fuel concentration is also important, although the minimum AIT's of most combustibles do not vary greatly with the fuel-oxidant ratio except at the near critical ratios for flame propagation, that is, near the lower and upper concentration limits of flammability. Vessels of approximately 200 cc (12.2 in³) volume or at least 2-inch diameter are usually adequate for most determinations in air at atmospheric pressure. However, larger size vessels are required at reduced oxygen concentrations. McDonald (Ref 22) reported that steel vessels of about 6-inch diameter are required to obtain the lowest possible AIT for materials with characteristics similar to kerosine. The ignition criterion is also important in comparing the AIT's of combustible materials. Figure 3 shows that with visible flame as the criterion, the minimum AIT (755°F) of the MIL-L-7808 dibasic acid ester oil in air (1 atm) increases markedly when cylindrical or spherical Pyrex vessels of less than 2-inch diameter are used. With sudden pressure rise as the ignition criterion, the minimum AIT of this lubricant is between 150° to 250°F lower in 3-inch diameter or larger cylindrical steel vessels. For maximum safety, the lowest AIT values should be used. Most of the 1-atmosphere AIT data presented in this report were obtained with visible flame as the ignition criterion; where other criteria were used, they are specified.

The vessel wall material and its surface condition can also influence the autoignition of combustible materials. The lowest AIT's are frequently found in glass or stainless steel vessels which have been conditioned by prior ignitions. However, the autoignition of some combustibles is more sensitive than others to the vessel material. Table 8 lists the AIT values found for the MIL-L-7808 engine oil in air with 1/2-inch diameter tubes of various materials. Note that a lower AIT value was obtained with this lubricant in a Pyrex tube than in a stainless steel or aluminum tube. No ignitions occurred in the copper tube since its surface oxidized and deteriorated greatly at the temperature required for ignition. In comparison, Figure 4 shows that the AIT of the MIL-O-5606 hydraulic fluid (mineral oil) varied only slightly with vessel material at reduced and elevated pressures; here, seven different materials were used. The variation of AIT with vessel material, vessel size, and other important variables is further illustrated in the subsequent sections of this report for the different classes of lubricants.

TABLE 8. Effect of Vessel Material on the Autoignition Temperature of MIL-L-7808 Engine Oil in Air at Atmospheric Pressure.

Cylindrical Vessels - 1/2-inch ID, 6 inches long
Ignition Criterion - Flame

	Vessel Material			
	Pyrex	Stainless Steel	Aluminum	Copper
AIT, °F ^{1/}	940	1015	1090	No ignition

^{1/} Minimum AIT in 213 cc spherical Pyrex vessel (2.93-inch ID) is 755°F.

2. Variation of Ignition Delay with Autoignition Temperature

The autoignition temperature of a flammable mixture depends to a large extent upon the length of time that the mixture is in contact with the heated walls of a vessel or with the surfaces of other heat sources. Since lubricants are used under static and dynamic conditions, it is of interest to know the variation of AIT with different contact times. Ordinarily, the contact times are referred to as ignition delays when ignition takes place. Figure 5 shows such data obtained at this laboratory (Ref 7) in quiescent air at atmospheric pressure for new and used samples of the dibasic acid ester oil (MIL-L-7808) and the polyol ester oil (MIL-L-9236). Note that ignition delays increase with decreasing temperature and tend to reach a maximum value at the lowest AIT of each oil. The maximum delay for both aircraft engine oils was under 10 sec, which is less than the maximum (>>10 sec) frequently found at the lowest AIT for many combustibles.

Similar data are shown for these lubricants injected into quiescent air at 1000 and 2000 psi oil pressures (Figure 6) and under flow conditions at 200 psi oil injection pressure (Figure 7). Here, ignition delays less than 1 sec were possible. Although AIT's are higher under flow conditions, they do not always differ greatly from those under static conditions when the fuel contact times or ignition delays are comparable (Ref 7). However, for the lubricants in Figures 6 and 7, the agreement is poor between the various sets of data.

With increasing pressure, ignition is more readily achieved and the fuel contact time required for ignition at a given temperature is lower. An example of this behavior is shown in Figure 8 for an aromatic ether engine lubricant (Monsanto MCS-293) in air at pressures from 1/4 to 4 atmospheres; note that at approximately 950°F (510°C), which is the minimum AIT at 1/2 atmosphere, the ignition delays decrease from 12 to 5 seconds

with a pressure increase to 4 atmospheres. It is also shown that the maximum ignition delays at the minimum AIT condition are much higher at the higher pressures where the AIT's are lower. Similar results are expected for other lubricants. Generally, the maximum ignition delays in quiescent air at atmospheric pressure range between 5 to 20 seconds for many lubricating materials, including the mineral oils.

3. Autoignition Temperatures at Various Injection Pressures and Spray Conditions

Many combustible fluids when projected against a heated surface at high fluid pressures ignite in air at temperatures lower than their minimum AIT's. Such information for lubricating fluids is important since they may be sprayed at high pressures onto heated surfaces as a normal operation; similar situations may arise as a result of a ruptured oil seal or hydraulic line in compressors, aircraft engines, and in other systems in which lubricants are used. Zabetakis, Furno, and Miller (Ref 2) have shown that the autoignition temperatures of some hydraulic fluids in air at atmospheric pressure vary noticeably with fluid injection pressure to critical values above which injection pressure has little effect. Figure 9 shows this data for seven hydraulic fluids which were injected into a Pyrex vessel (200 cc) with a diesel injector at fluid pressures to 5000 psig; data at zero injection pressure correspond to those obtained in minimum AIT determinations with a hypodermic syringe. At zero injection pressure, the minimum AIT's range between 700° and 800°F for all the fluids except the MIL-H-5606 whose value is 440°F. The minimum AIT's for the diester- (MLO 54-581) and silicate-type (MLO 54-856, MLO 8200, MLO 54-645, MLO 54-540) hydraulic fluids decrease markedly as the injection pressure is increased up to about 500 psig; with a further increase of injection pressures, the AIT's vary little. In comparison, the data for the chlorinated silicone fluid (MLO 53-446) and the mineral oil (MIL-H-5606) are independent of injection pressure to 5000 psig. It is also seen that the chlorinated silicone fluid has much higher AIT values than the other hydraulic fluids at injection pressures greater than about 500 psig.

As previously shown in Figure 4, the minimum AIT of the MIL-H-5606 fluid at zero injection pressure is affected only slightly by the composition of the heated surface. The effect of surface composition is also reported to be unimportant for this fluid at various injection pressures (Ref 3). However, the AIT's of hydraulic fluids like the MLO 53-446 and MLO 54-581 may be lower in metal vessels than in Pyrex vessels by as much as about 50°F, depending on the metal composition and injection pressure (Figures 10 and 11). Catalytic surface reactions are frequently suggested to explain such results, but the efficiency of heat transfer from the different heated surfaces to the injected liquid may also be important.

The effect of injection pressure on autoignition temperature is further illustrated in Figure 12 for three aircraft engine oils which were injected into a 500 cc Vycor flask (Ref 7). The data for a polyphenyl ether oil (5P4E), which has a very high AIT (>1100°F) in air, are

essentially independent of injection pressure between 0 and 2000 psig. In comparison, the data for the polyol ester (MIL-L-9236) and sebacate ester (MIL-L-7808) oils display somewhat the same effect of injection pressure as observed for most of the hydraulic fluids having comparable AIT's. As with the latter hydraulic fluids, the AIT's did not decrease when the injection pressure was greater than 500 psig.

Frank, Swarts, and Mecklenburg (Ref 12) have also compared autoignition temperatures of various synthetic lubricants and hydraulic fluids in air by spray-injection and dropwise addition (by hypodermic syringe) methods. A comparison of the results is given in Table 9 for data obtained with siloxanes, halogenated hydrocarbons, and various silicate, phosphate, and organic esters. Generally, there is little difference between the values obtained by both methods for most of the materials. Only the silicate and organic esters (diisooctyl adipate and diethylene glycol benzoate 2-ethyl hexanoate) ignited at noticeably lower temperatures by the spray-injection method as compared to the drop method used. These three materials and trihexyl phosphate have low AIT's compared to the other lubricants examined, particularly the halogenated hydrocarbon fluids.

Goodall and Ingle (Ref 21) also demonstrated that the sprays or highly atomized droplets of the dibasic acid ester oil (MIL-L-7808D) ignite at hot plate temperatures lower ($>100^{\circ}\text{F}$) than those required with liquid jets or slightly atomized droplets. However, their results for a hydraulic mineral oil indicated little effect of fluid atomization. The authors suggested that the AIT of the more viscous and less volatile oil (MIL-L-7808D) decreases with increased atomization because the number of small oil droplets on the heated surface is greater and this results in increased rates of heat transfer and vaporization. Although the Bureau of Mines data at increased injection pressure are also indicative of the effect of increased atomization, those for the very high viscosity oil (5P4E - Figure 12) and for most of the low viscosity hydraulic fluids (Figure 9) are not consistent with the above suggestion. According to the available data, the AIT's of the lubricants with very high (e.g. $\sim 550^{\circ}\text{F}$) or very low flash points (e.g. $\sim 200^{\circ}\text{F}$) appear to be influenced little by injection pressure or degree of atomization; those with intermediate flash point values display the greatest variation in autoignition temperature behavior with such injection variables.

TABLE 9. Comparison of Autoignition Temperatures of Lubricants and Hydraulic Fluids in Air at Atmospheric Pressures by Spray Injection and Dropwise Addition Methods.¹⁷

Material	Spontaneous Ignition Temperature, °F			
	Spray Injection		Dropwise Addition	
	Air Flow, 7.6 in ³ /min	Quiescent Air	Air Flow, 7.6 in ³ /min	Quiescent Air
(2-ethylhexyl) silicate (Orsil B.F-1; Oronite Chem.Co.)	475	518	570	570
(2-ethylhexyl) silicate + 1 percent phenyl-beta-naphthylamine (Orsil B.F.-1-S; Oronite Chem.Co.)	492	487	570	570
Dimethyl siloxane (10 centistokes at 25°C) (DC-200 series; Dow Corning Corp.)	704	702	705	705
Dimethyl siloxane (50 centistokes at 25°C) (DC-200 series; Dow Corning Corp.)	806	812	834	837
Diisooctyl adipate (Plexol-244; Rohm & Haas Co.,Inc.)	549	580	690	712
Diethylene glycol benzoate 2-ethylhexoate (Hooker Electrochemical Co.)	522	530	644	662
Diocetyl isooctene phosphonate (Victor Chemical Works)	624	625	607	605
Diocetyl benzene phosphonate (Victor Chemical Works)	600	600	597	599
Trihexyl phosphate (Shell Development Co.)	547	549	---	---
Tricresyl phosphate (Monsanto Chemical Co.)	1112	1112	1110	1110
Arochlor - 1248 (Monsanto Chemical Co.)	1184	1180	1185	1185
Arochlor - 1254 (Monsanto Chemical Co.)	1104	1087	1104	---

Table 9 (Cont)

Material	Spontaneous Ignition Temperature, °F			
	Spray Injection		Dropwise Addition	
	Air Flow, 7.6 in ³ /min	Quiescent Air	Air Flow, 7.6 in ³ /min	Quiescent Air
Trichloro-1-(pentafluoroethyl) -4-(trifluoromethyl) benzene	1054	1054	<u>2</u> /	<u>2</u> /
Dichloro-1-(chlorotetrafluoroethyl) -4-(trifluoromethyl) benzene	1095	1089	<u>2</u> /	<u>2</u> /
3-chloro-(trifluoromethyl) benzene	1210	1205	<u>2</u> /	<u>2</u> /
Fluorolube F-S (polytrifluorochloroethylene)	1205	1205	<u>2</u> /	<u>2</u> /
Tetrachloro decafluoro-heptanes	1217	1217	<u>2</u> /	<u>2</u> /

1/ Data from Ref 12.

2/ Spontaneous ignition temperature obtained by dropwise addition is similar to that obtained by spray addition.

4. Autoignition Temperatures in Various Oxygen-Nitrogen Atmospheres

The autoignition of lubricants in oxygen-nitrogen atmospheres involves oxidation reactions whose rates are dependent on the temperature, pressure, and the concentration and composition of the combustible and oxidant materials. Generally, the AIT's of most combustible materials are lower at atmospheric pressure than at reduced pressures; also, they are lower in oxygen than in air. Figures 13 and 14 show such data for the series of seven hydraulic fluids discussed in the previous section of this report. The AIT's of six of the fluids in Figure 13 increase between 200° and 600°F with a decrease of initial pressure from 1 to 1/4 atmosphere; the MIL-H-5606 mineral oil data display the greatest pressure dependency. In comparison, the AIT behavior of the chlorinated silicone base fluid (MLO 53-446) is affected only slightly over this pressure range. It is also interesting to note that the order of the AIT's for the MLO 53-446 (highest) and MIL-H-5606A (lowest) fluids at 1 atmosphere is reversed at the lower pressures. Furthermore, these two fluids show no effect of oxygen concentration (21 to 100 percent) on their autoignition temperatures, whereas the results for the other five fluids display a noticeable effect. The AIT's of the latter five materials decreased markedly as the oxygen content increased to about 50 percent, above which little variation occurred. A comparison of the data in Figures 9 and 14 shows that the variation of AIT with increasing injection pressure is similar to that observed with increasing oxygen concentration for each of the hydraulic fluids used.

In the experiments discussed above, autoignition was detected by the presence of flame. When a sudden pressure rise is the ignition criterion, the effect of initial pressure and oxygen concentration on the AIT is less pronounced. Figures 15 and 16 show that the AIT's of the MIL-L-7808 dibasic acid ester oil and MIL-L-9236 polyol ester oil vary only slightly with initial pressure (1/4 to 5 atmospheres) and oxygen concentration (10 to 100 percent) when pressure rise is the ignition criterion; the high AIT polyphenyl ether oil (5P4E) and the naphthenic mineral oil (MLO-7277) behave similarly over the range of test conditions examined. However, when visible flame is the ignition criterion, the AIT's are noticeably higher in air than in oxygen. An additional point of interest is that the reaction temperature corresponding to a sudden pressure rise in air for the MIL-L-7808 oil (486°F) is essentially the same as its decomposition temperature (490°F, Table 2).

Similar data on the effect of initial pressure or oxygen concentration are shown in Figure 17 for two organic ester oils (TP 653B and P/O) and in Figure 18 (Monsanto MCS-293) and Figure 19 (Monsanto OS-124) for two aromatic ether lubricants. The AIT's for these materials also are not greatly pressure or oxygen concentration dependent if pressure rise is the ignition criterion and vessel size or surface is not a factor. Generally, the available data indicate that most lubricants require rather high temperatures for ignition in air at highly reduced pressures (< 1/4 atm), or

in oxygen-nitrogen mixtures at greatly reduced oxygen concentrations (< 5 percent) and atmospheric pressure. It has also been observed that the AIT values for some lubricants in various oxygen-nitrogen atmospheres can be correlated on the basis of the oxygen partial pressure (P_{O_2}). The data for the MCS-293 lubricant (Figure 18) have been found to fit the following expression:

$$AIT = a + \left[b/P_{O_2} \right]^{3/2} \quad (2)$$

where a and b are constants and P_{O_2} is the oxygen partial pressure in atmospheres or in other appropriate units. Thus, the AIT of this lubricant is inversely proportional to the $3/2$ power of the oxygen partial pressure. The variation of AIT with oxygen partial pressure is shown in Figure 20 for several of the combustible fluids; this figure includes data from Figures 13 to 19 obtained at various initial pressures and oxygen concentrations. It is evident that the AIT's of the mineral oil and silicate ester hydraulic fluids are the most dependent on oxygen partial pressure (P_{O_2}) while those for the sebacate and polyol esters are the least dependent on P_{O_2} . The results for the aromatic ethers and the phosphate ester fluids display an intermediate P_{O_2} dependence compared to those of the above fluids.

Although AIT data for the lubricants are useful in assessing possible explosion hazards associated with the use of the materials, the data obtained in air at moderate pressures cannot be relied upon for applications at elevated pressures. In some applications, the pressures of interest may be as high as 15,000 psig; for example, some air compressors are designed to operate at these high pressures. Since maximum explosion pressures can be as high as about eight times the initial pressure, or even much higher in the event of a detonation, the importance of knowing the AIT behavior of lubricants under these conditions cannot be overemphasized. Figure 21 shows the variation of AIT with pressure to 200 atmospheres (3000 psia) or more for three phosphate ester-base fluids, (Houghto-Safe 1055 and 1120, and Cellulube 220) a phosphate ester-chlorinated hydrocarbon mixture (Pydraul AC), two mineral oils (MIL-2190 and Harmony 44), and a water-glycol fluid (Houghto-Safe 271); these data were obtained by Zabetakis, Scott, and Kennedy (Ref 5) with an abrupt pressure rise as the ignition criterion, except at atmospheric pressure where ignition was detected by the appearance of flame. The AIT's for all the fluids decrease with an increase in pressure, although they tend to level off at pressures equal to or greater than approximately 100 atmospheres. In fact, the values for the MIL-2190 oil even increase slightly with increased pressure at the higher test pressure and nearly approximate the values for some of the phosphate ester lubricants; possible variations in fluid injection pressures may account for this unexpected behavior. It is also noted that the four phosphate ester fluids consistently required higher temperatures for ignition than the other fluids, but that the differences were less noticeable at the higher pressures.

Similar data recently obtained by the present authors are presented in Figure 22 for the MIL-L-7808, Mobil DTE-103, and Houghto-Safe 1055 lubricants at pressures up to 15,000 psig. An abrupt pressure rise was the ignition criterion for all of the determinations. Again, the AIT's decreased with increased pressure to some critical value above which the pressure effect was negligible. The critical values were about 300 atmospheres for the phosphate ester base (Houghto-Safe 1055) and petroleum base (Mobil DTE-103) oils and about 100 atmospheres for the sebacate ester oil (MIL-L-7808).

The AIT's of these materials differ less noticeably at the higher test pressures, although the phosphate ester lubricant had the highest AIT. Differences between some of the AIT data for this lubricant in Figures 21 and 22 can be attributed to possible differences in fluid injection pressures; also, the ignition criterion for the 1 atmosphere data was not the same in each study. The data, summarized in Table 10 for the above three lubricants, indicate that the minimum AIT's at atmospheric pressure can be much lower ($\geq 150^{\circ}\text{F}$) for the Houghto-Safe 1055 and MIL-L-7808 lubricants when pressure rise, rather than visible flame, is the ignition criterion; the difference is not as pronounced for the Mobil DTE-103 lubricant.

Table 10 also lists the ignition delays and maximum pressure rises observed at the minimum AIT conditions in these experiments. Although all the data were not consistent, both the ignition delays and pressure rises increased with decreasing AIT, i.e. with increasing initial pressure. In some of the experiments with the Mobil DTE-103 mineral oil at 10,000 psig, the pressure rises were above 50,000 psi and sufficient to rupture the 1/8-inch ID stainless steel tubing (heavy wall) which was employed. It is possible that the other two lubricants may also develop such high pressures under the same test conditions if the combustible-air ratio is favorable. Further investigation should be conducted to explore this possibility with various classes of lubricants.

In Table 11, the various classes of lubricants are compared according to the approximate order of their minimum AIT's in air at atmospheric pressure; the data in Table 2 were used for this comparison. Since the minimum AIT's and decomposition temperatures do not differ greatly for many lubricants (see Table 2), the order of their AIT's is somewhat comparable to the order of their thermal stability indicated in Table 3. The aromatic ether and aromatic phosphate ester fluids are among the materials having the highest AIT and are followed by the halogenated and nonhalogenated silicones. However, the halogenated hydrocarbon based fluids also have very high AIT's but have low thermal stability. Another exception are the mineral oils, some of which had the lowest AIT but which have relatively fair stability. The aliphatic phosphate ester fluids, which have poor stability, also rank among materials with lowest AIT's. Since many lubricants are only grossly defined and may also contain significant quantities of additives, AIT and decomposition temperature data should be determined for the basic chemical compounds of these materials to obtain a more meaningful comparison of the data.

TABLE 10. Minimum Autoignition Temperatures of Houghto-Safe 1055, Mobil DTE-103, and MIL-L-7808 Lubricants in Air at Various Initial Pressures.

Initial Pressure, psig	Oil Volume, cc	AIT's °F	Ignition Delay, sec	Pressure Rise, psi	Ignition Criterion
<u>Houghto-Safe 1055</u>					
0	0.5	1022	--	--	Flame ^{1/}
0	0.5	832	49	2	Pressure rise ^{2/}
500	2	765	61	100	" "
1000	6	635	55	200	" "
2000	6	605	25	100	" "
5000	7	500	193	8500	" "
10000	7	490	213	9500	" "
15000	12	470	160	17000	" "
<u>Mobil DTE-103</u>					
0	0.1	702	--	--	Flame ^{1/}
0	0.6	675	25	3	Pressure rise ^{2/}
500	4	630	101	100	" "
1000	4	535	7	500	" "
2000	6	520	25	300	" "
5000	7	415	56	7500	" "
10000	7	400	25	10000	" "
15000	7	395	247	10000	" "
<u>MIL-L-7808</u>					
0	0.5	728	--	--	Flame ^{1/}
0	0.6	565	11	3	Pressure rise ^{2/}
500	4	495	142	400	" "
1000	6	420	115	1000	" "
2000	6	400	260	2000	" "
5000	4	390	188	11000	" "
10000	7	375	206	20000	" "
15000	12	370	288	35000	" "

^{1/} 500 cc Vycor Vessel - 0 psig data.

^{2/} 260 cc Cylindrical Stainless Steel Vessel - 0 to 2000 psig data.

273 cc Cylindrical Steel Vessel - 5000 to 15000 psig data.

TABLE 11. Approximate Minimum Autoignition Temperature Range of Various Classes of Lubricants.

<u>AIT Range</u>	<u>Lubricant Class</u>
1000-1200°F	Halogenated Hydrocarbons Aromatic Ethers Aromatic Phosphate Esters
800-900°F	Silicones Halogenated Silicones
700-800°F	Water-Glycols Aliphatic Silanes Hydrocarbon Polyol Esters Sebacate Esters Mineral Oils Aliphatic Silicate Esters
400-550°F	Aliphatic Phosphate Esters Mineral Oils

COMPARISON OF AUTOIGNITION, WIRE IGNITION AND HOT GAS IGNITION TEMPERATURES

Most autoignition temperature data are primarily applicable to situations in which a flammable mixture contacts a relatively large heated surface, such as the walls of a tank. Ignition may also result in small heated containers or tubes and in situations where the heat source is a heated wire or a jet of hot gas; jets of hot air, oil vapor or other gases can be produced as a result of a pinhole leak or an oil seal failure in various lubricating systems, including those of an aircraft engine. The size and shape of the heat source are important in both hot gas and hot surface ignitions. Accordingly, it is of interest to compare the temperature requirements for ignition with various heat sources and as a function of the dimensions of the heat source.

Like heated vessel or autoignition temperatures, wire ignition temperatures decrease with increasing wire diameter. For MIL-L-7808 vapor-air mixtures at atmospheric pressure, the following empirical expression was found by the authors (Ref 8) to describe the approximate variation of the wire ignition temperatures (T , °R) with wire radius (r) between 0.008 and 0.375-inch; 2-inch lengths of Nichrome wires or rods were used with

optimum oil vapor-air mixtures for ignition:

$$\log_e r = 25800/T - 18.53 \quad (3)$$

At the smallest wire radius (0.008-inch), the ignition temperature is over 1500°F and much higher than the minimum AIT (755°F) of this lubricant in a 200 cc vessel with visible flame as the ignition criterion. However, these ignition temperatures do not differ so greatly when the sizes of the heat sources are comparable. For example, the ignition temperatures were 1015°F with a wire of 0.375-inch radius and 835°F with a cylindrical Pyrex tube (6-inch length) of the same radius.

The agreement between ignition temperatures is improved when differences in heat source lengths are considered and the data are plotted as a function of the surface area of the heat sources (Figure 23). Figure 23 includes data for the MIL-L-7808 engine oil, a JP-6 jet fuel, and three paraffinic hydrocarbons. It is not surprising that only the data for the engine oil correlated over the entire range of heat source surface areas, since the oxidation reactions involved are primarily of the high temperature type for this material having a high AIT ($\geq 750^\circ\text{F}$). In comparison, the data for the materials with low AIT's ($\geq 400^\circ\text{F}$) reflect low and high temperature oxidation reactions; therefore, the sudden changes in the slopes of the curves for these fuels may be attributed to transitions from "cool" or "blue" flame ignitions to normal ignitions. Petroleum base oils would be expected to display somewhat the same behavior. The ignition temperatures of the engine oil are lower than those of the hydrocarbon fuels when the heat source surface area is equal to or less than about 10 in², that is, at temperatures greater than about 900°F. Apparently, at these temperatures, the adipate-sebacate esters which make up this oil break down to form more thermally unstable species than those formed by the four hydrocarbon fuels. Thus, the ignition temperature behavior of lubricants at high temperatures cannot be predicted from their thermal stability at low temperatures. The following expression approximates the variation of ignition temperature (T, °F) of the MIL-L-7808 oil in atmospheric air with surface area (A, sq.in.) of the heated Nichrome wires or rods and Pyrex vessels:

$$T = 1175 - 115 \log_e A; \quad 0.1 < A < 29 \quad (4)$$

In oxygen, the wire and vessel ignition temperatures would be about one half those predicted by the above equation.

The hot gas ignition temperatures of combustible vapor-air mixtures also decrease with an increase in the diameter of the heat source. Figure 24 compares the minimum ignition temperatures of the MIL-L-7808 engine oil and the JP-6 hydrocarbon fuel (vapor-air mixtures) obtained using heated Pyrex vessels, Nichrome wires or rods, and jets of hot air of various diameters. The hot gas ignition temperatures are generally higher

than the hot surface ignition temperatures; however, they tend to converge as the heat source diameter is increased, indicating that little difference should be expected between these ignition temperatures at source diameters greater than about 1 inch. Also, one should expect the heated vessel ignition temperatures to be higher than those possible with heated wires or jets of hot air when the source diameter is nearly equivalent to the critical tube diameter for flame propagation; for hydrocarbon fuels, the critical tube diameter is approximately 0.1 inch in air at 1 atmosphere (Ref 39). Figure 24 also shows the range of heat source diameter over which the dibasic acid ester oil can have lower hot gas and hot surface ignition temperatures than the JP-6 fuel, which has a low AIT in large heated vessels.

IGNITION BY SHOCK WAVES AND ADIABATIC COMPRESSION

The ignition of a lubricant vapor-air mixture can also result from heating the mixture to its ignition temperature by compression or by propagation of a shock wave through the mixture. Ignitions by such pressurization may occur in reciprocating engines, compressor lines, and in other systems where the gaseous mixtures are subject to compression. Even the sudden opening of a valve connecting a high and low pressure system may result in a shock wave which is capable of igniting a flammable oil vapor-air mixture that is present. The theoretical gas temperatures which can result from shock wave and adiabatic compression are compared in Table 12 from Ref 40 for various compression ratios (P_2/P_1). According to these values, shock wave compression ratios equal to or greater than about 10 are required to produce localized temperatures which are comparable to the minimum AIT's of most of the lubricants in air at atmospheric pressure; similarly, compression ratios equal or greater than about 50 are required in the case of adiabatic compression. However, the temperature required for ignition will depend greatly upon the duration of heating and the rate of heat loss to the environment. Thus, relatively strong shock waves ($P_2/P_1 \gg 10$) would normally be required to ignite the lubricant vapor-air mixtures.

Perlee and Zabetakis (Ref 6) have discussed the problems of compressor and related explosions and have shown how the rate of pressurization and pipe dimensions may influence the ignition of phosphate-ester base fluids and mineral-oil base fluids at various compression ratios. Figures 25 and 26 show data presented by these authors based on the investigations at the Penn State University (Ref 41) and the Electric Boat Division of General Dynamics Corporation (Ref 42). The results in Figure 25 indicate that the rate of pressure rise required for ignition increases sharply below some critical compression ratio for each lubricant; also, the rate required is greater for the phosphate-ester base fluid and can be as much as 1000 times greater in a 3/8-inch diameter pipe than in one of 2-inch diameter. As one would expect, the rate of pressure rise or the compression ratio required for ignition increases with a decrease of initial temperature (Figure 26). The rate of required pressure rise also tends to decrease

with increasing tube length. At the same time, it is important to remember that the maximum rates of pressure rise or flame propagation normally increase with increasing tube length and that the normal explosion (deflagration) may convert to a detonation. Such detonations have been shown to be possible using films of oil or grease in steel tubes of only 0.8-inch diameter (Ref 43); the detonations occurred within 25 tube diameters from the ignition source.

TABLE 12. Compressed Gas Temperatures at Various Compression Ratios.^{1/}

Compression Ratio P_2/P_1	Temperature of Compressed Gas, °F	
	T ₂ , Shock Wave	T ₂ , Adiabatic Compression
2	144	134
5	406	206
10	810	467
50	3610	970
100	6490	1250
1000	33940	2615
2000	51540	3255

^{1/} Table from Ref 40.

As in most ignition processes, the presence of certain contaminants or decomposition products can influence the ignition temperature behavior of lubricants in compressor type systems. For example, Lenhard (Ref 44) and Loison (Ref 45) reported that certain iron oxides may be present and lower the ignition temperatures of the oil vapor-air mixtures in the system. Similarly, Busch, Berger and Schrenk (Ref 46) suggest that carbonaceous deposits from an air compressor can decompose or react with air to possibly initiate an explosion. In any event, ignition can only occur if sufficient quantities of the combustibles, oil or carbonaceous deposits, are present to form flammable mixtures in the given oxidant atmosphere. Therefore, proper maintenance is necessary to prevent excessive accumulation of combustibles or possible catalysts and, thus, minimize the hazards of operating any system employing combustible lubricants. The various precautions which have been mentioned in this report and elsewhere (Ref 6) must be considered to help insure safe operations of both low and high pressure lubricating systems.

SUMMARY

A compilation of ignition temperature, flammability, and other related data are presented for over 90 lubricants, engine oils, and hydraulic fluids. The concepts of ignition and flame propagation are discussed and the various environmental factors which can influence the potential fire or explosion hazards associated with the combustible fluids are illustrated. The variation of the minimum autoignition temperatures (AIT's) of such fluids in heated vessels is shown as a function of oxygen concentration from 5 to 100 percent and initial pressure from 1/8 to 1000 atmospheres. Similarly, data are given on the dependence of the AIT's on vessel size, vessel material, injection pressure, and heating time or ignition delay; static and dynamic conditions are considered. Ignition temperatures obtained in heated vessels are also compared to those associated with ignitions by heated wires or rods, jets of hot gases, shock waves, and adiabatic compression. In addition, flammability data are included for the fuel vapor-oxidant mixtures and sprays or mists formed by the lubricants in oxygen-nitrogen atmospheres. An approximate order is indicated for the various chemical classes of lubricants with respect to their temperature requirements for autoignition, decomposition, and formation of flammable vapor-air mixtures.

The review of the literature has revealed that there is little information on the lubricants for predicting the ignition hazards which can arise from their spontaneous heating (slow oxidation). Work in this problem area is warranted since many oil fires are reported to have resulted from the spontaneous heating of oil-soaked insulation at relatively low temperatures. Similarly, a need exists for information on the critical ignition and flame propagation parameters for the sprays and foams which can be generated by the lubricants under certain pumping conditions. Also, additional AIT data are needed on the polyester hydrocarbon lubricants and other lubricating fluids for which such information is lacking.

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MLO-56-578	--	5
MLO-56-582	--	6
MLO-56-610	--	6
MLO-56-611	--	6
MLO-5731	--	4
MLO-57-9	--	6
MLO-59-98	--	6
MLO-59-287	--	6
MLO-59-692	--	7
MLO-60-50	--	5
MLO-60-294	--	4
MLO-63-24	--	7
MLO-63-25	--	7
MLO-7277	--	4, 50
Mobil DTE-103	Mobil Oil Co.	4, 23, 57
Nyvac 20	"	4
Orsil B.F. 1	Oronite Chemical Co.	6, 18
Orsil B.F.-1-S	"	18
Oronite 8200 (MLO-8200)	"	6, 44, 48, 49, 55
Oronite 8515	"	6, 10, 37
OS-124	Monsanto Co.	7, 54, 55
Plexol 79	Rohm & Haas Co.	5
Plexol 201	"	5
Plexol 244	"	5, 18
Plexol 273	"	5
P/O (Esso 4275)	Esso Standard Oil Co.	5, 52
Pydraul AC	Monsanto Co.	5, 55, 56
Pydraul A-200	"	6
Pydraul F-9	"	5
Pydraul 150	"	5
Skydrol	"	5, 13
Tetra (2-ethylhexyl) Silicate	--	6
TP 653B	Heyden Newport	5, 52
Tricresyl Phosphate	Monsanto Co.	5, 13, 18
Trihexyl Phosphate	Shell Development Co.	5, 18
Trimethylolpropane tri- pelargonate	--	5
Trioctyl Phosphate	(Standard Oil Development Co.	5, 13
	(Shell Development Co.	

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<u>Lubricant</u>	<u>Vendor</u>	<u>Page</u>
Ucon 50HB-260	Carbide & Carbon Chemical Corp.	4
Ucon 50HB-280-X	"	4, 13
Ucon LB-60	"	4
Ucon LB-400-X	"	4, 13
Versilube F-44	General Electric Co.	6
Versilube F-50	"	6
mm-4P4E	--	7
mm-5P4E	--	7
5P4E	--	7, 47, 50, 51
pppp-6P5E	--	7

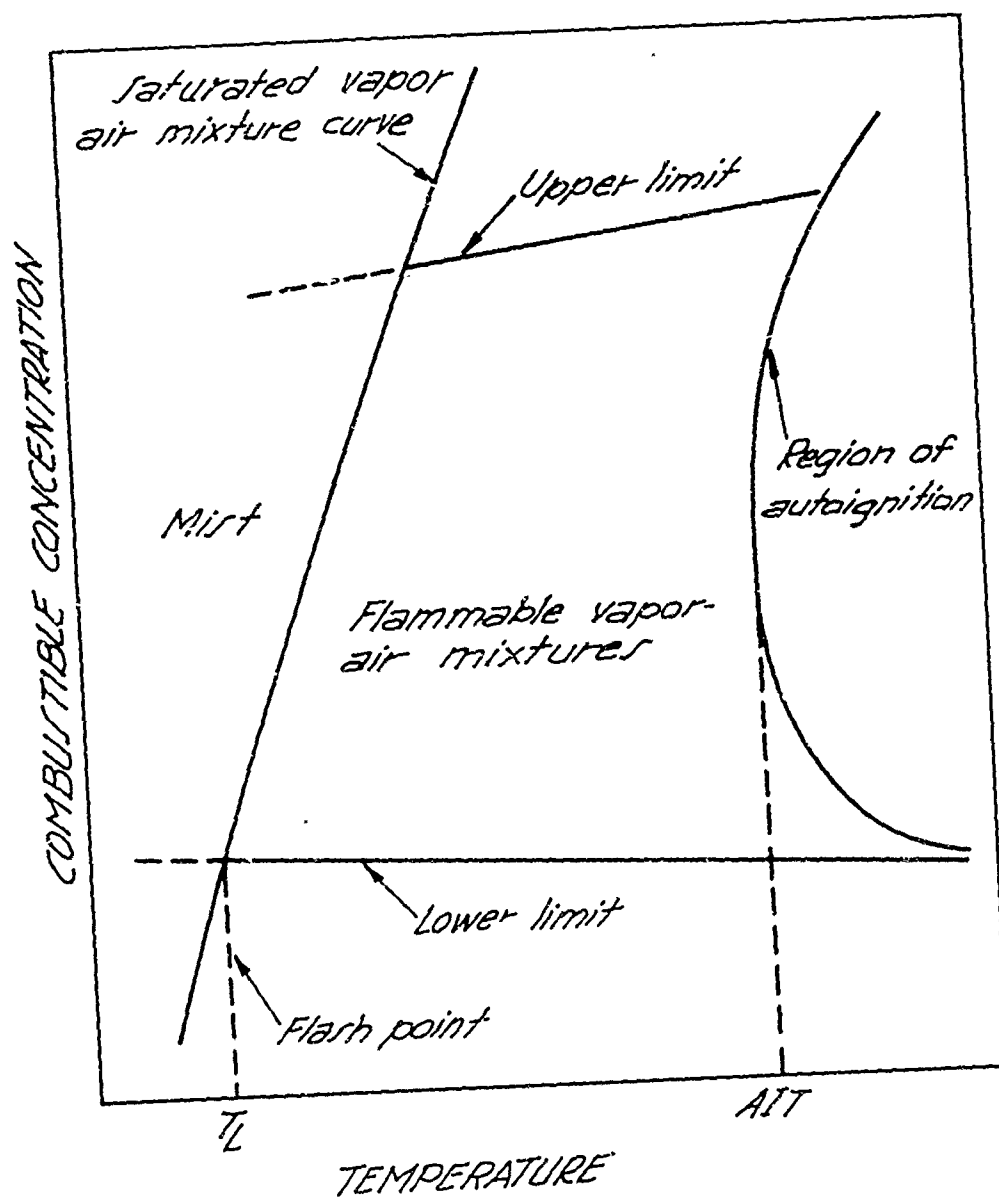


Figure 1. Effect of temperature on the limits of flammability of a combustible vapor in air at a constant initial pressure.

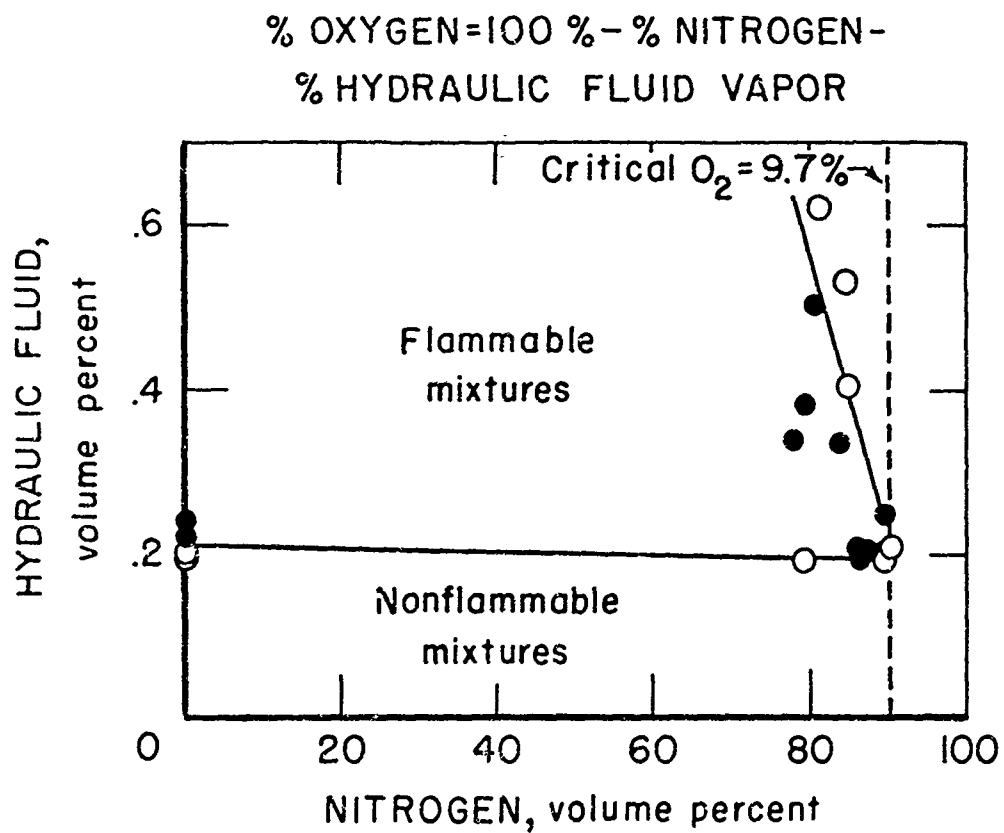


Figure 2. Partial flammability diagram for Oronite 8515 hydraulic fluid-oxygen-nitrogen mixtures at 550 °F and atmospheric pressure.

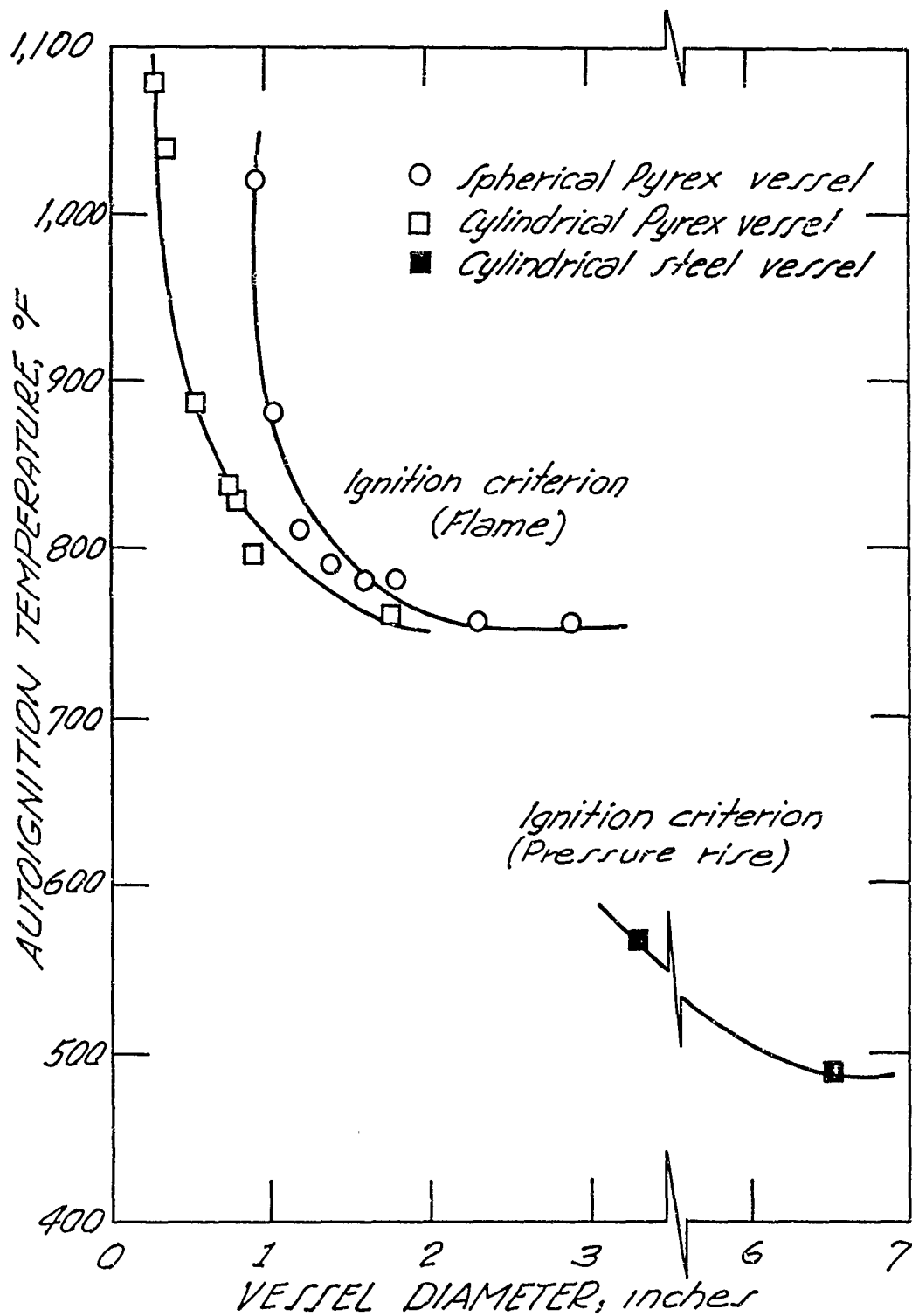


Figure 3. Minimum autoignition temperature versus vessel diameter for MIL-L-7808 engine oil in air at atmospheric pressure.

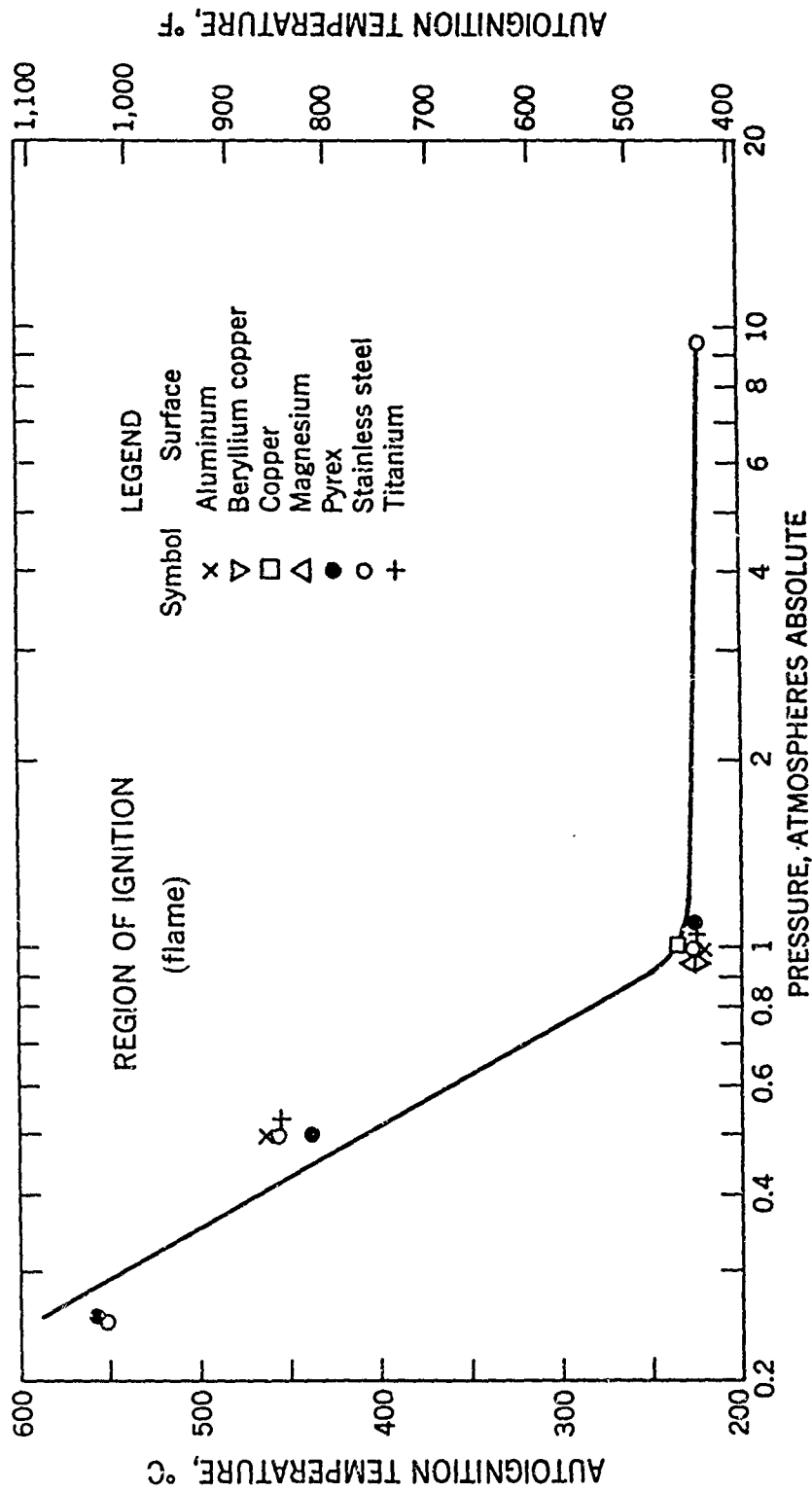


Figure 4. Minimum autoignition temperature of MIL-O-5606 in air in contact with various surfaces as a function of test chamber pressure. (200 cc Pyrex vessel, 380 cc stainless steel vessel, and 450 cc vessels for other materials).

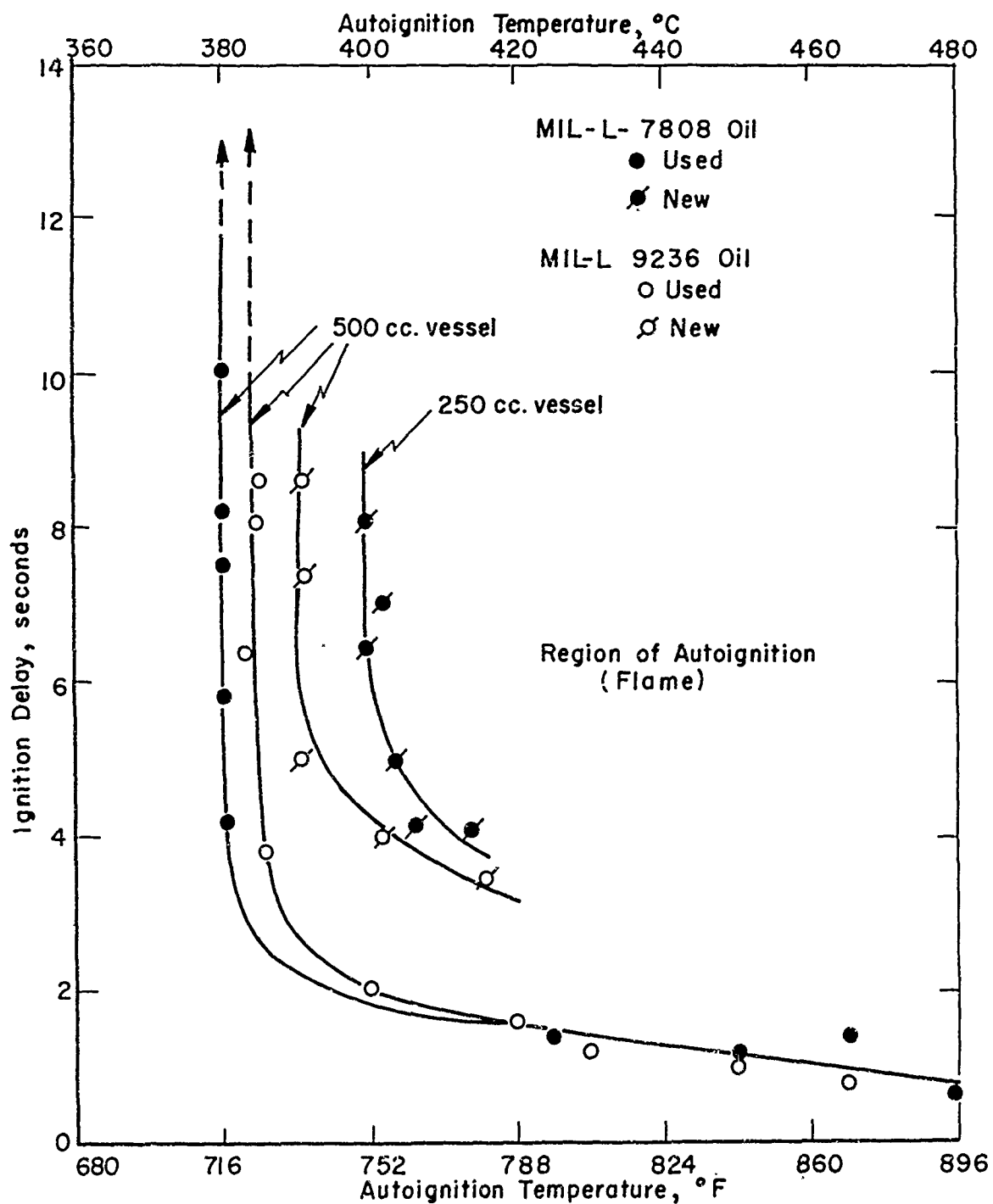


Figure 5. Variation of ignition delay with autoignition temperature of new and used engine oils (MIL-L-7808 and MIL-L-9236) in air at atmospheric pressure.

Open vessels - Vycor Erlenmeyers

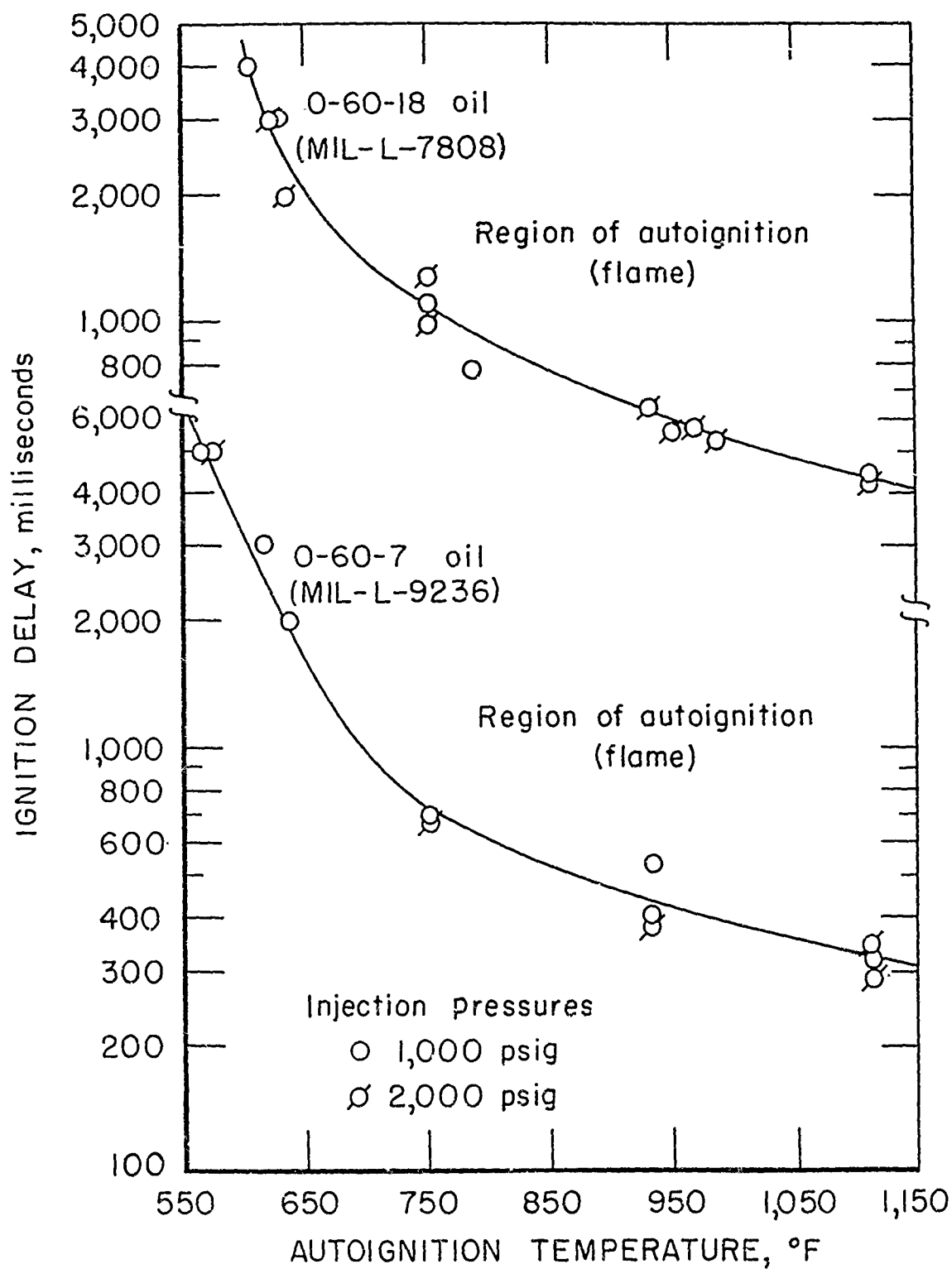


Figure 6. Variation of ignition delay with autoignition temperature for engine oils 0-60-7 and 0-60-18 in air at atmospheric pressure and at 1,000 and 2,000 psi injection pressures. (500 cc open Vycor Erlenmeyer, fuel volume ~ 0.2 cc).

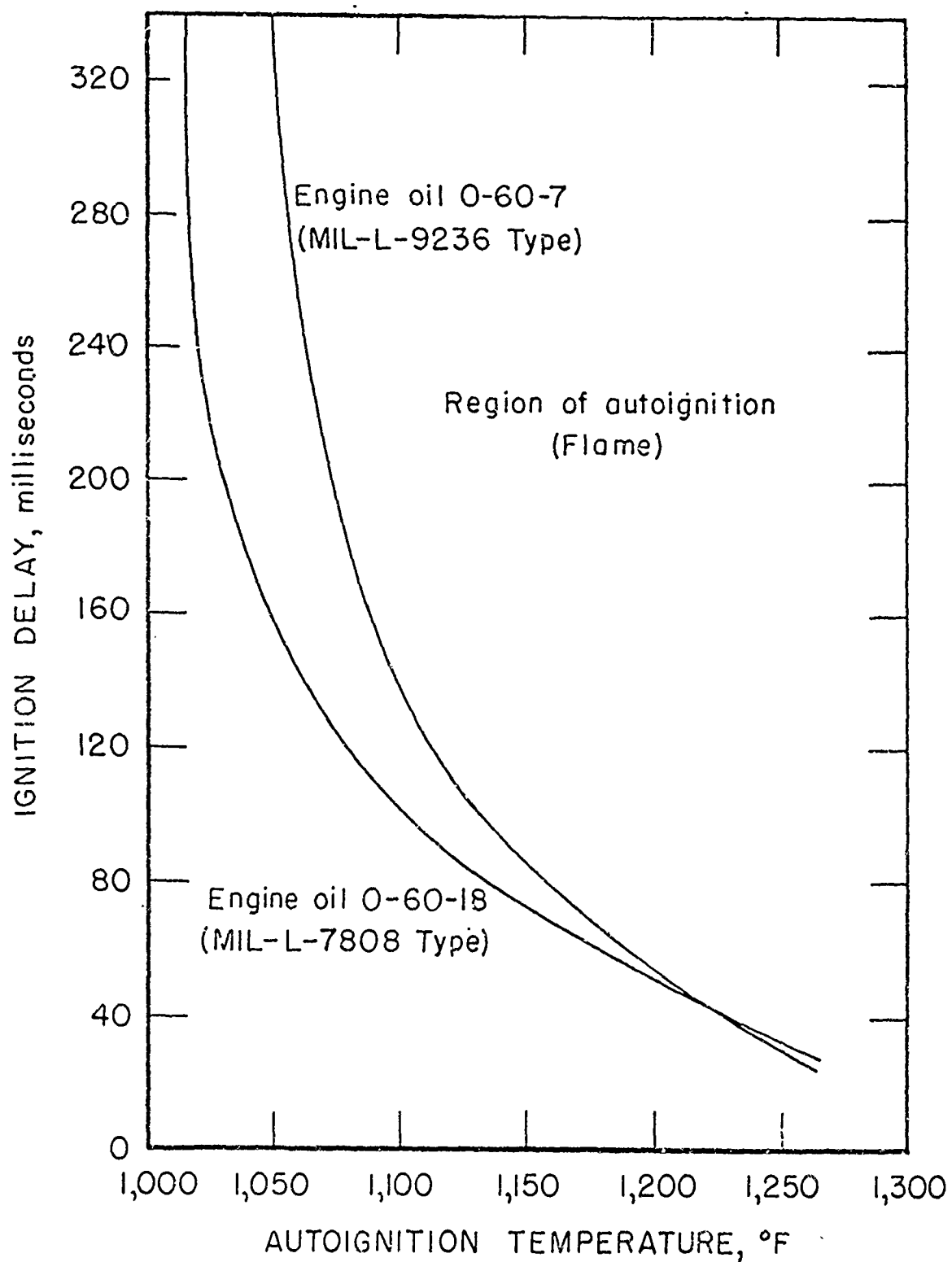


Figure 7. Variation of ignition delay with autoignition temperature for engine oils 0-60-7 and 0-60-18 in air under dynamic test conditions. (Combustion tube, 2-inch ID, chamber pressure, 2 and 5 psig).

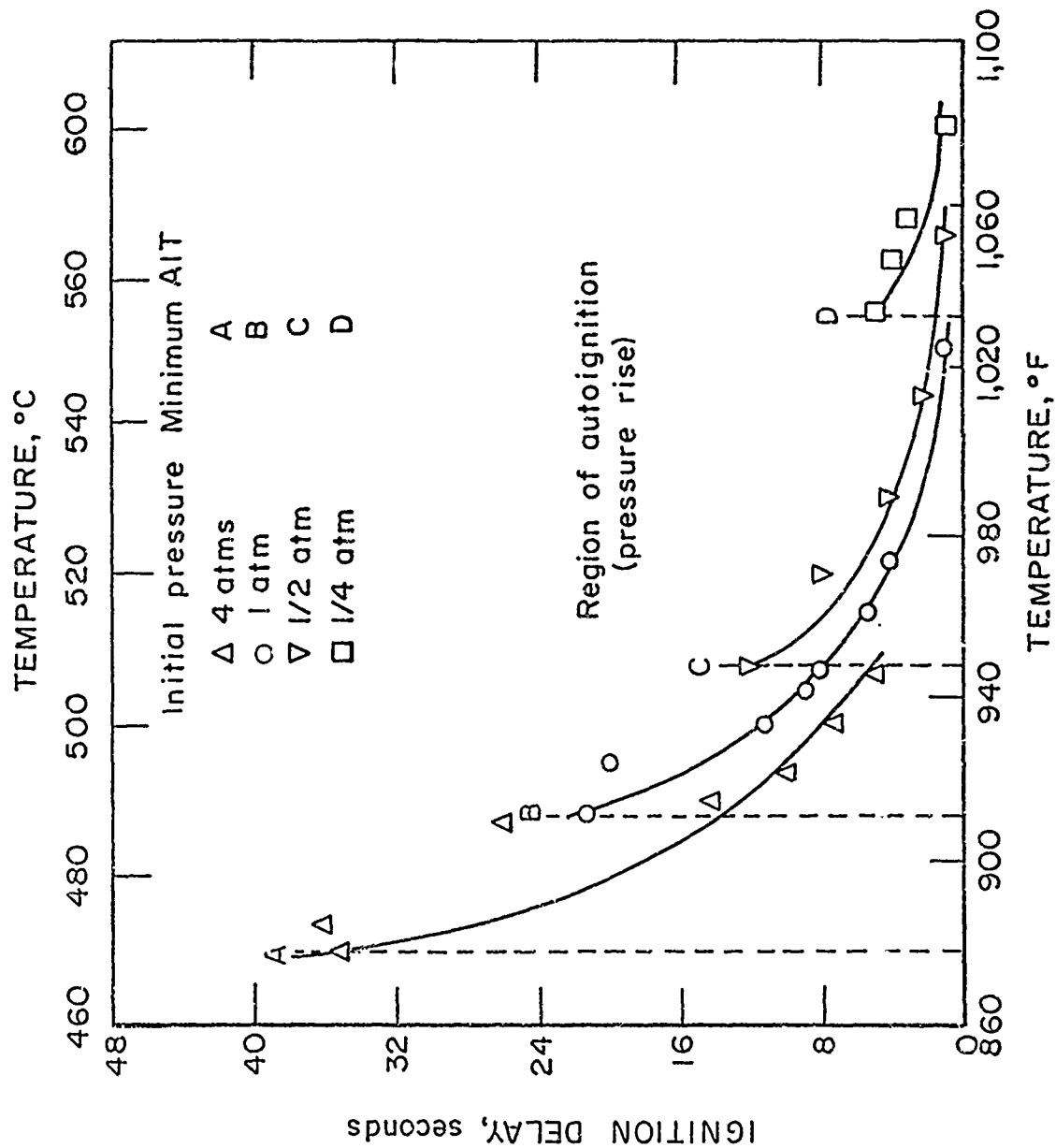


Figure 8. Variation of ignition delay with autoignition temperature of aromatic ether engine lubricant (Monsanto MCS 293) in air at various initial pressures (2540 cc stainless steel vessel).

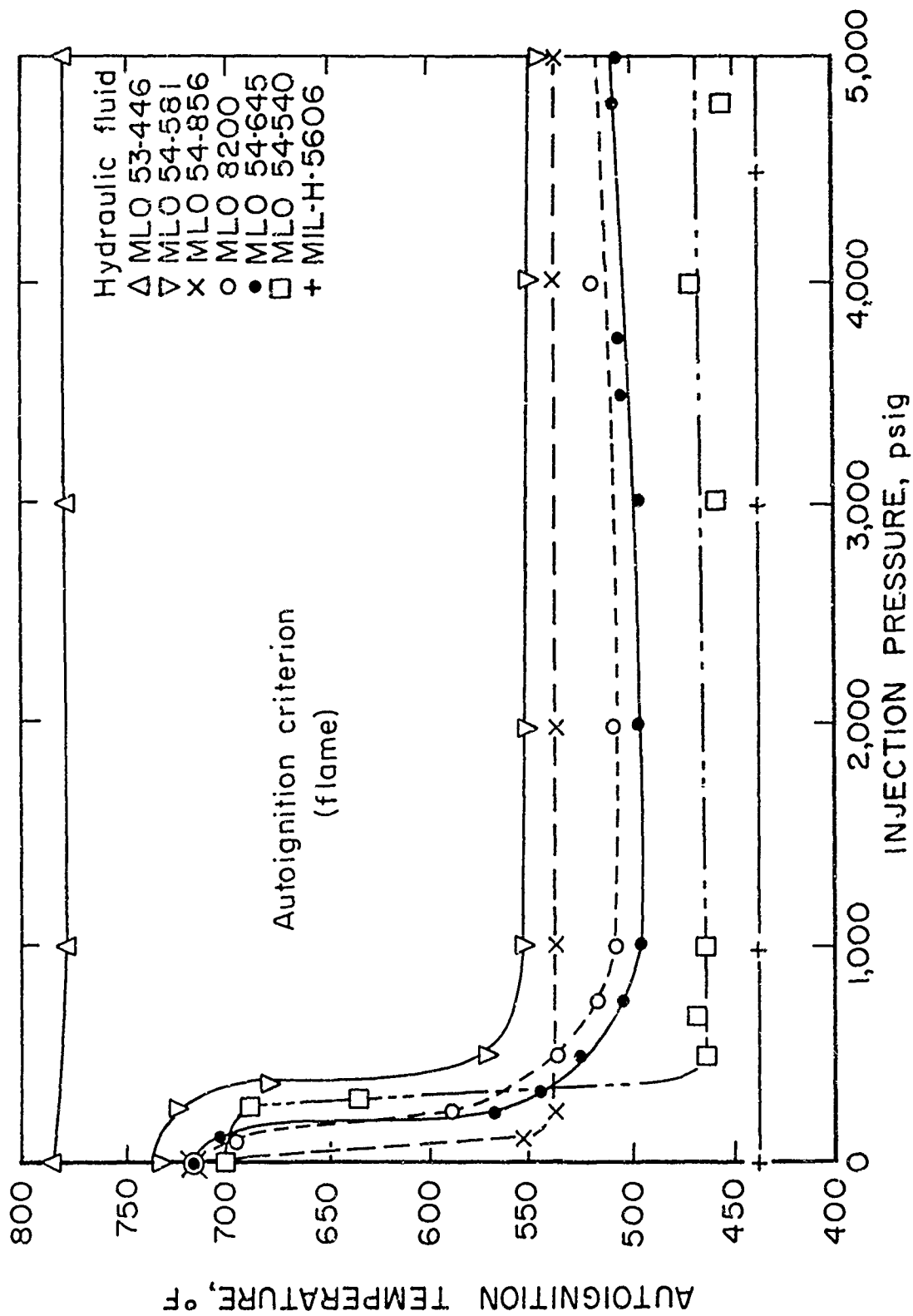


Figure 9. Minimum autoignition temperatures of seven hydraulic fluids in air at one atmosphere pressure in contact with a Pyrex glass surface as a function of diesel injector pressure (200 cc Pyrex vessel).

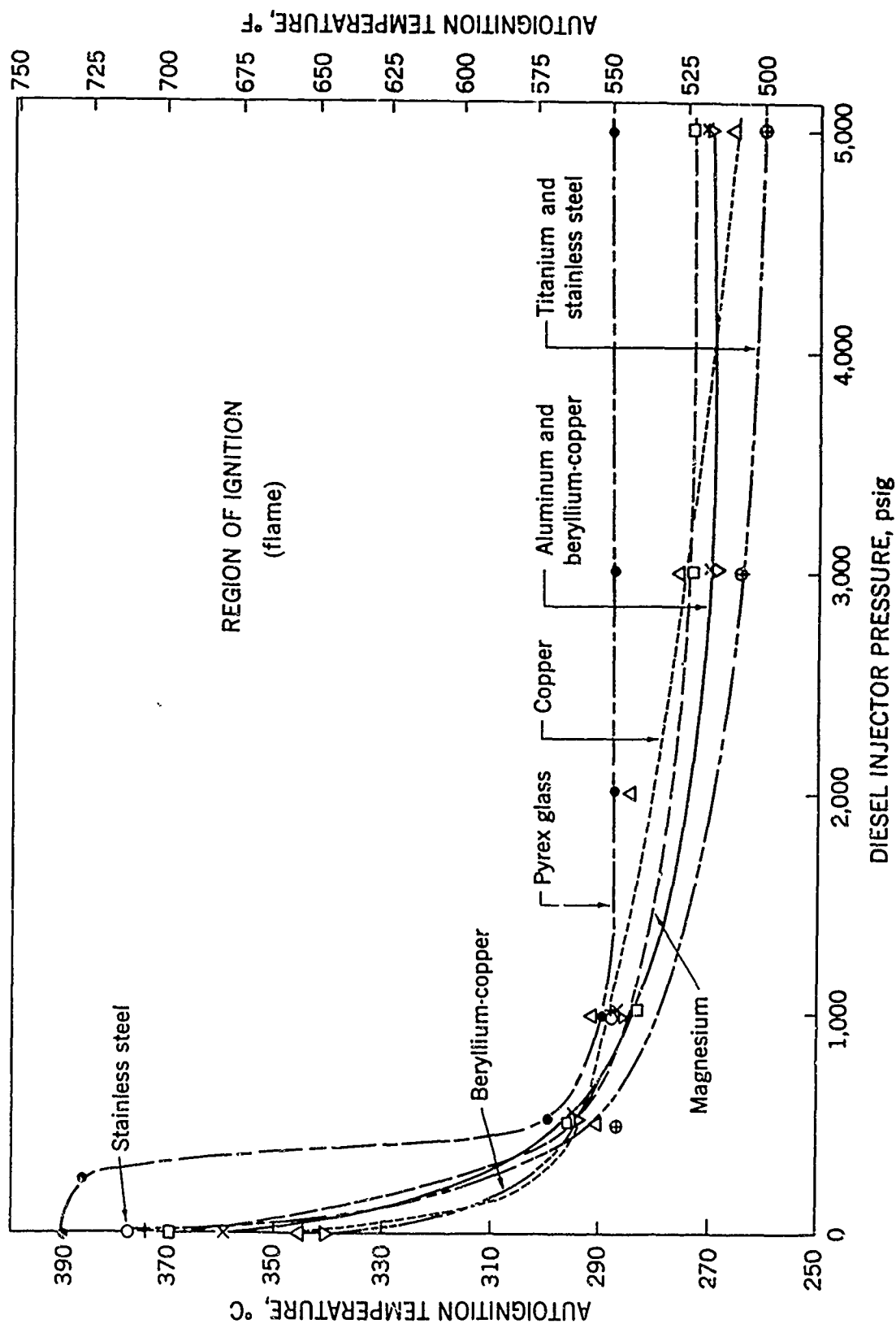


Figure 10. Minimum autoignition temperatures of MLO 54-581 hydraulic fluid in air at one atmosphere pressure in contact with various surfaces as a function of diesel injector pressure (200 cc Pyrex vessel, 380 cc stainless steel vessel, and 450 cc vessels for other materials).

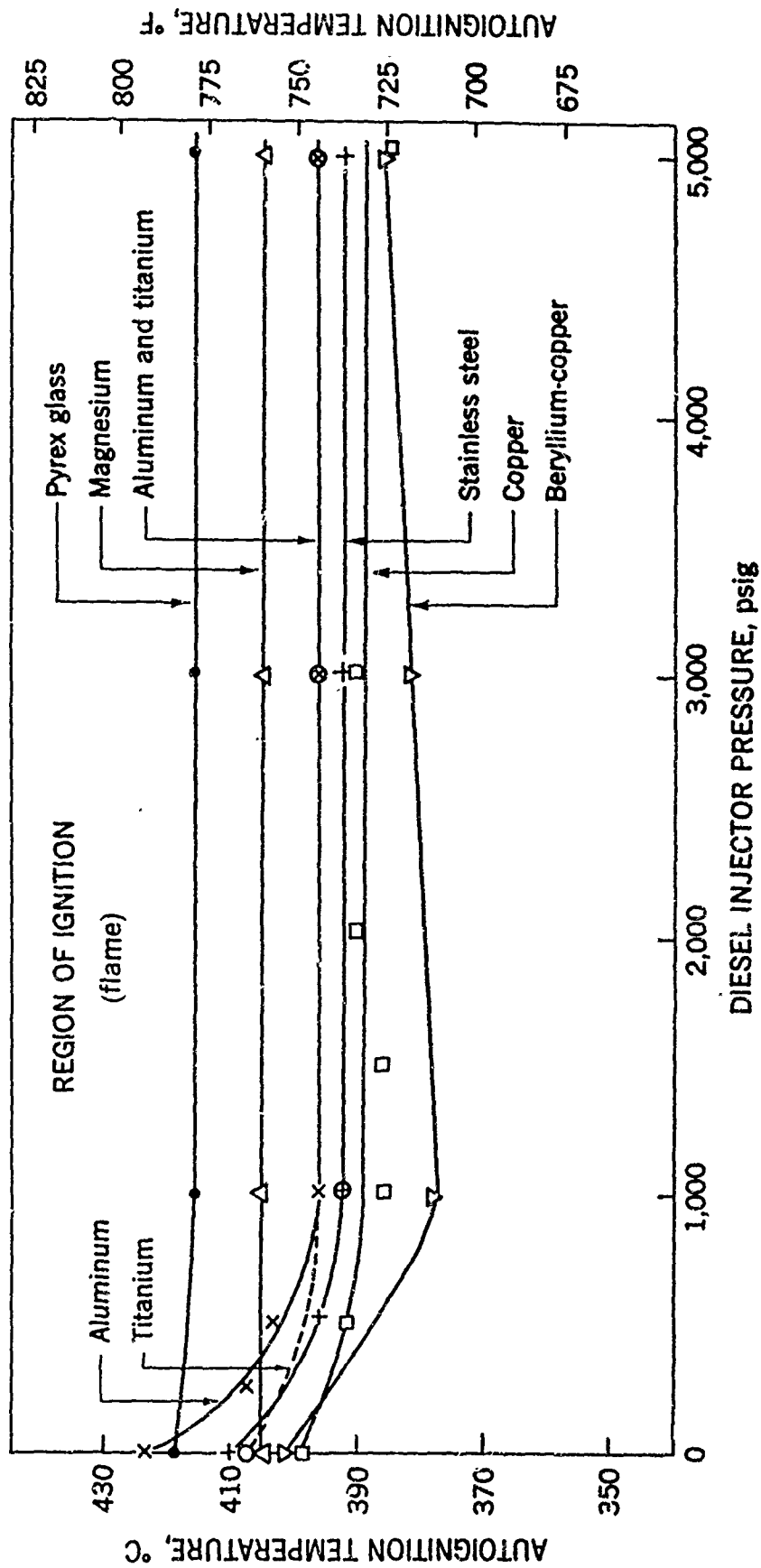


Figure 11. Minimum autoignition temperatures of MLO 53-446 hydraulic fluid in air at one atmosphere pressure in contact with various surfaces as a function of diesel injector pressure (200 cc Pyrex vessel, 380 cc stainless steel vessel, and 450 cc vessels for other materials).

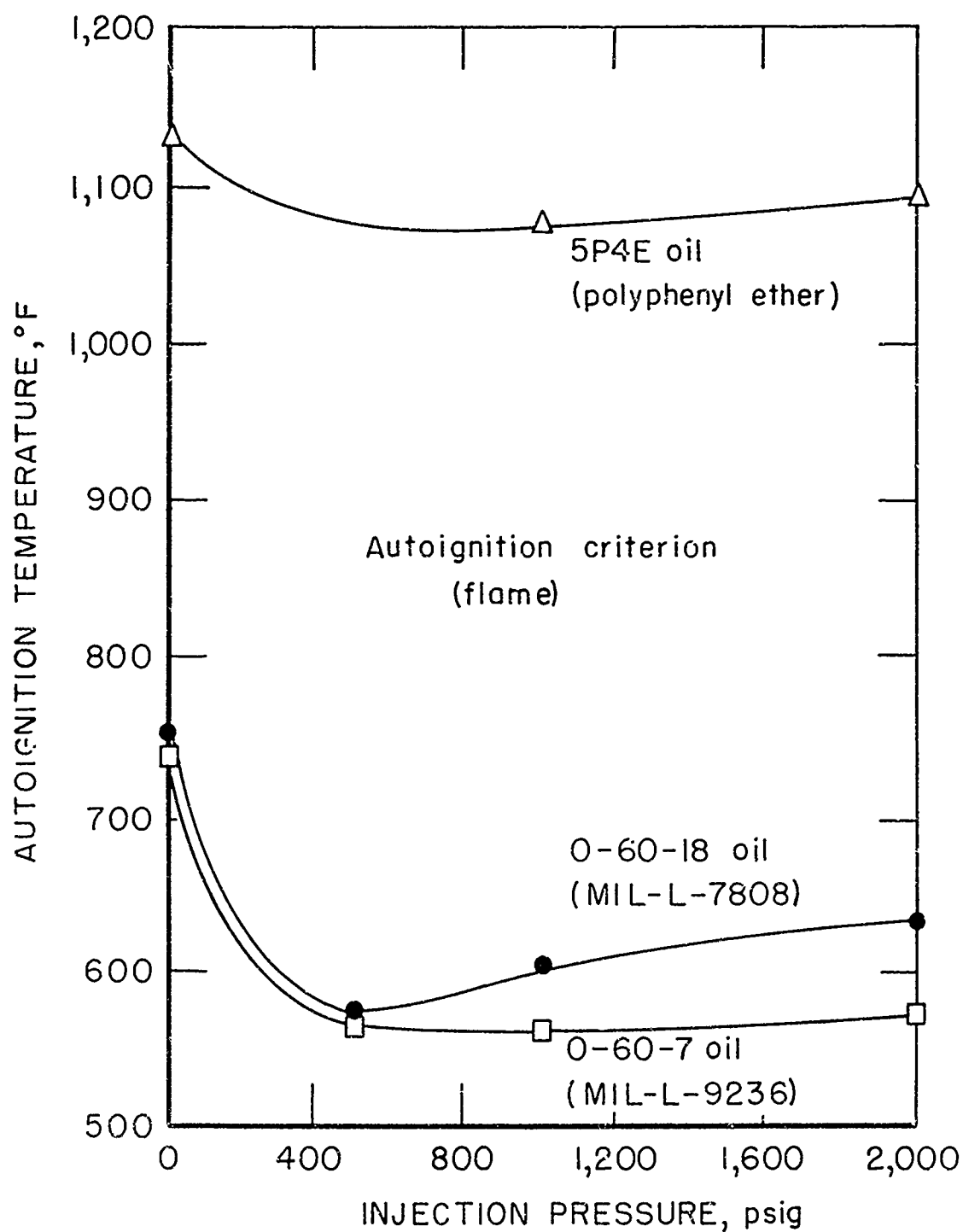


Figure 12. Autoignition temperatures of engine oils in air at atmospheric pressure and at various injection pressures (500 cc open Vycor Erlenmeyer, fuel volume - 0.05-0.30 cc).

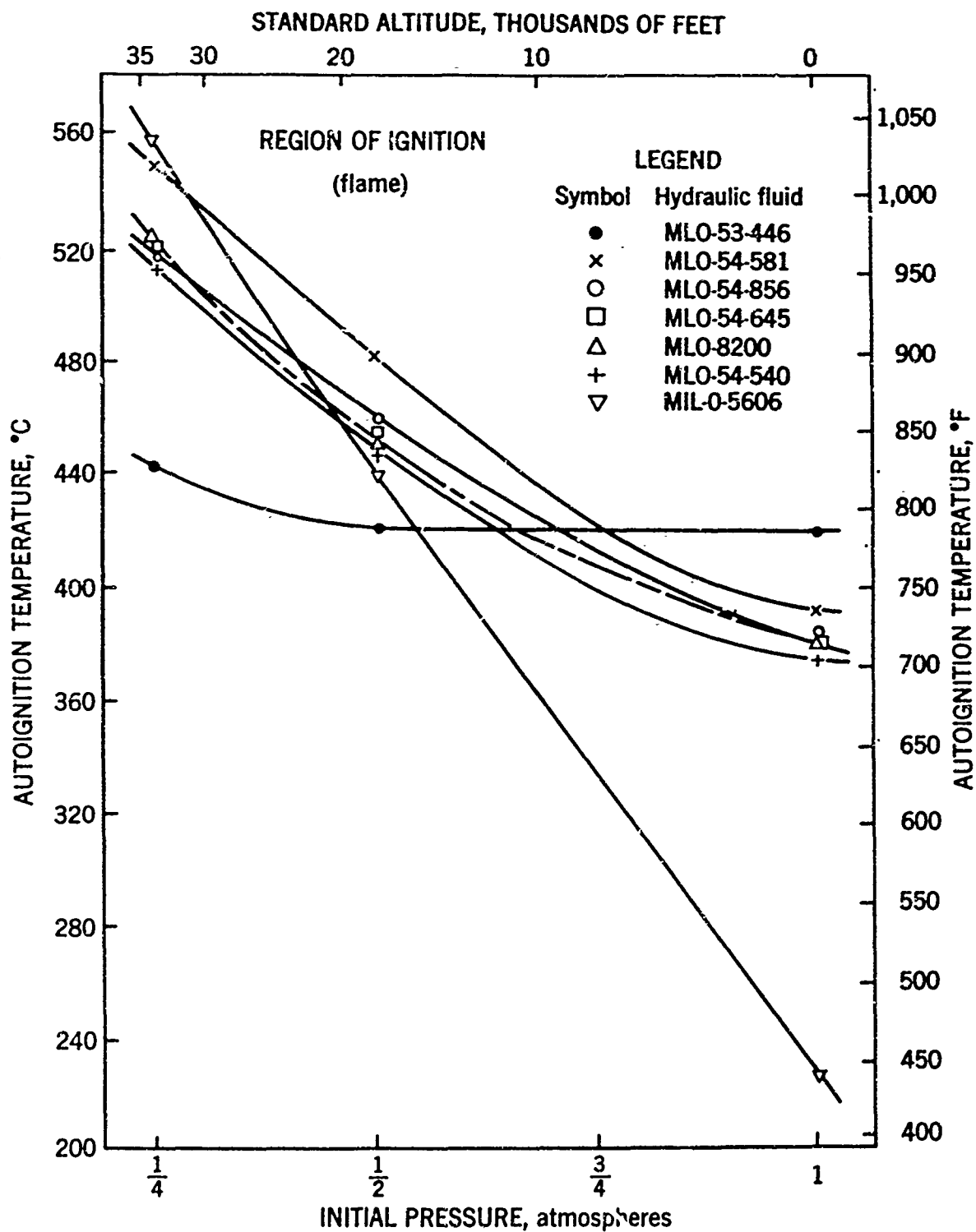


Figure 13. Minimum autoignition temperatures of seven hydraulic fluids in air in contact with a Pyrex glass surface as a function of test chamber pressure (200 cc Pyrex vessel).

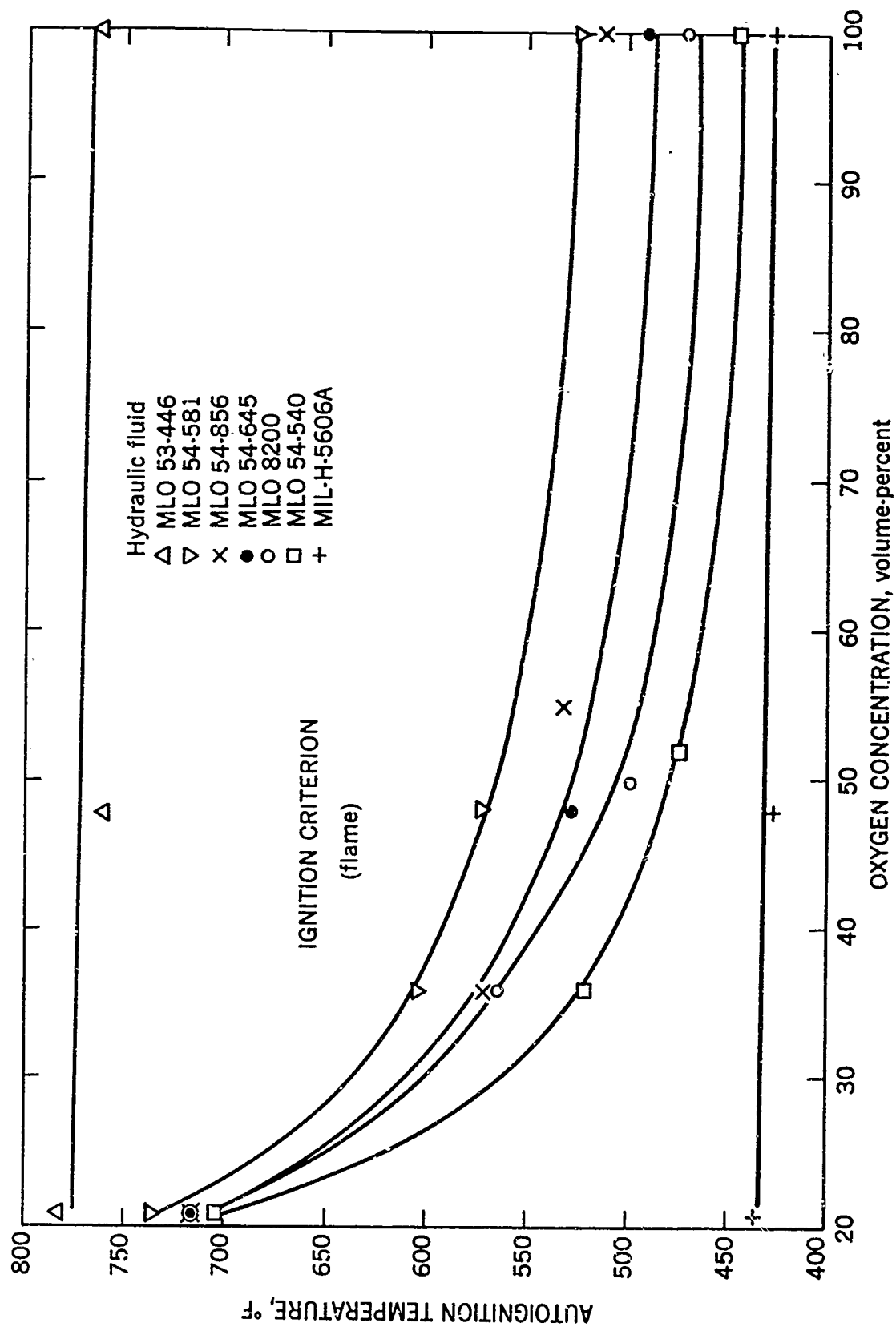


Figure 14. Minimum autoignition temperatures of seven hydraulic fluids in oxygen-nitrogen atmospheres at one atmosphere pressure in contact with a Pyrex glass surface as a function of oxygen concentration (200 cc Pyrex vessel).

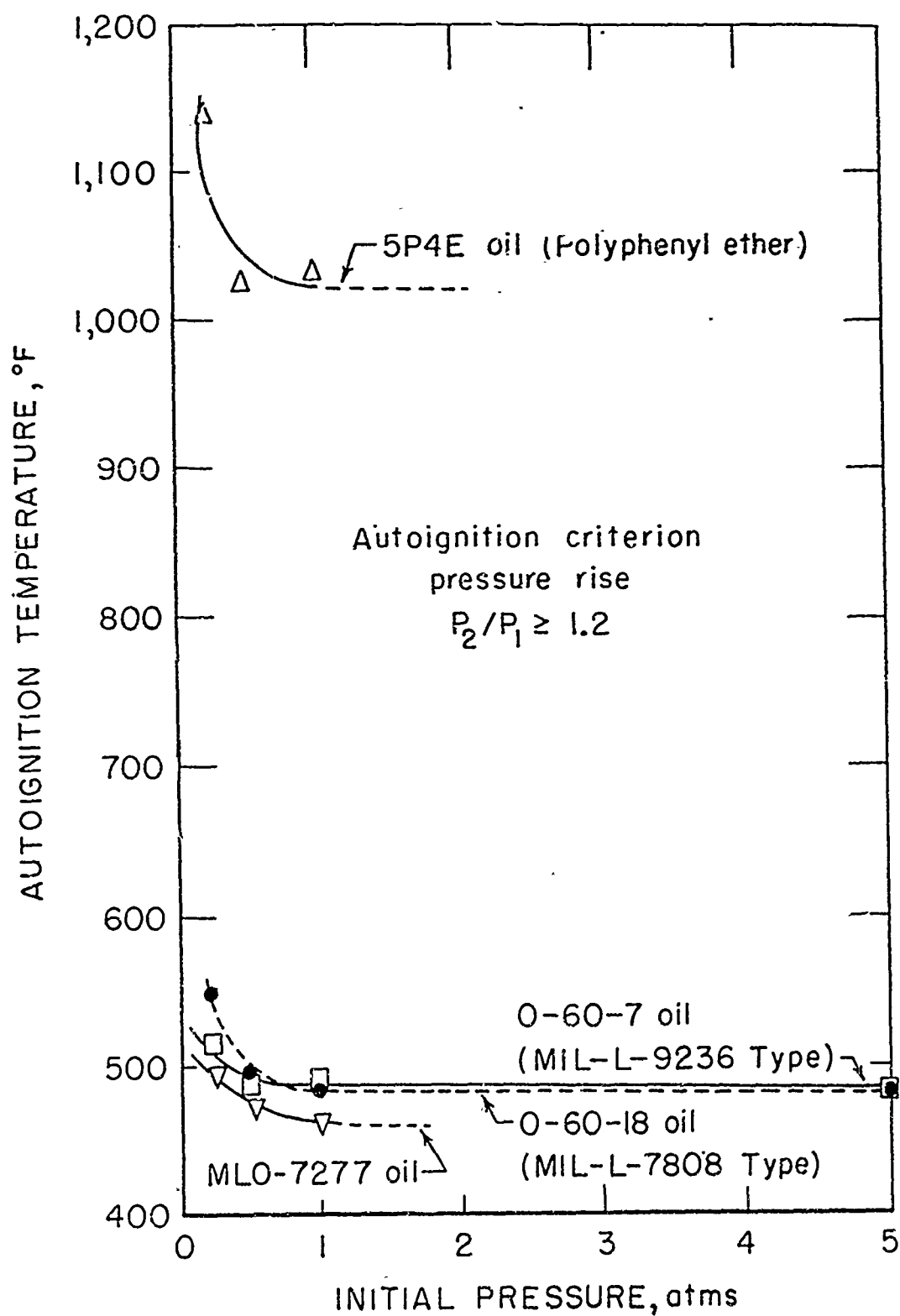


Figure 15. Minimum autoignition temperatures of engine oils in air at various initial pressures. (2,540 cc cylindrical steel vessel).

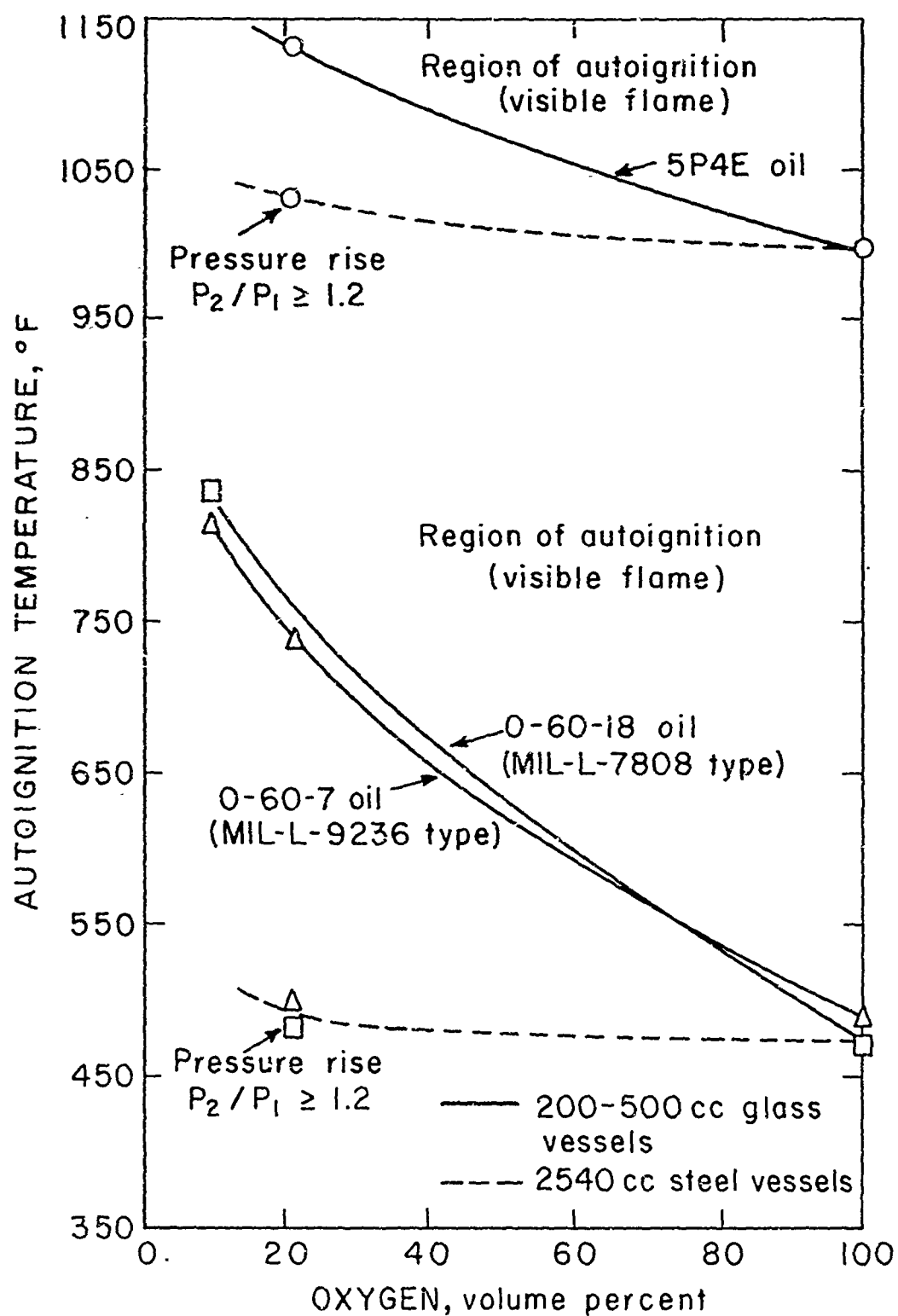


Figure 16. Minimum autoignition temperatures of engine oils at atmospheric pressure in various oxygen-nitrogen atmospheres in various size vessels.

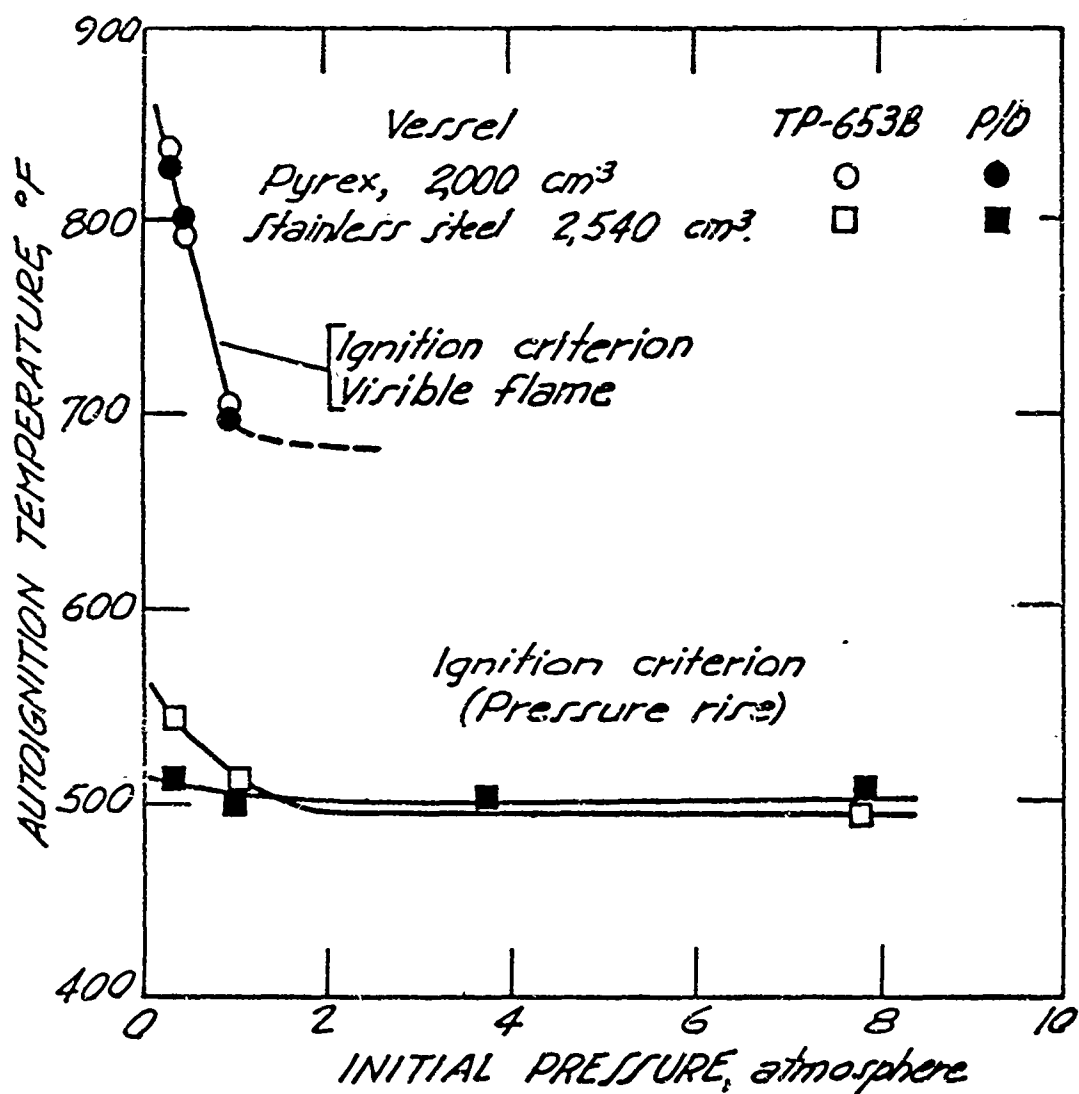


Figure 17. Minimum autoignition temperatures of TP 653B and P/O engine oils in air at various initial pressures.

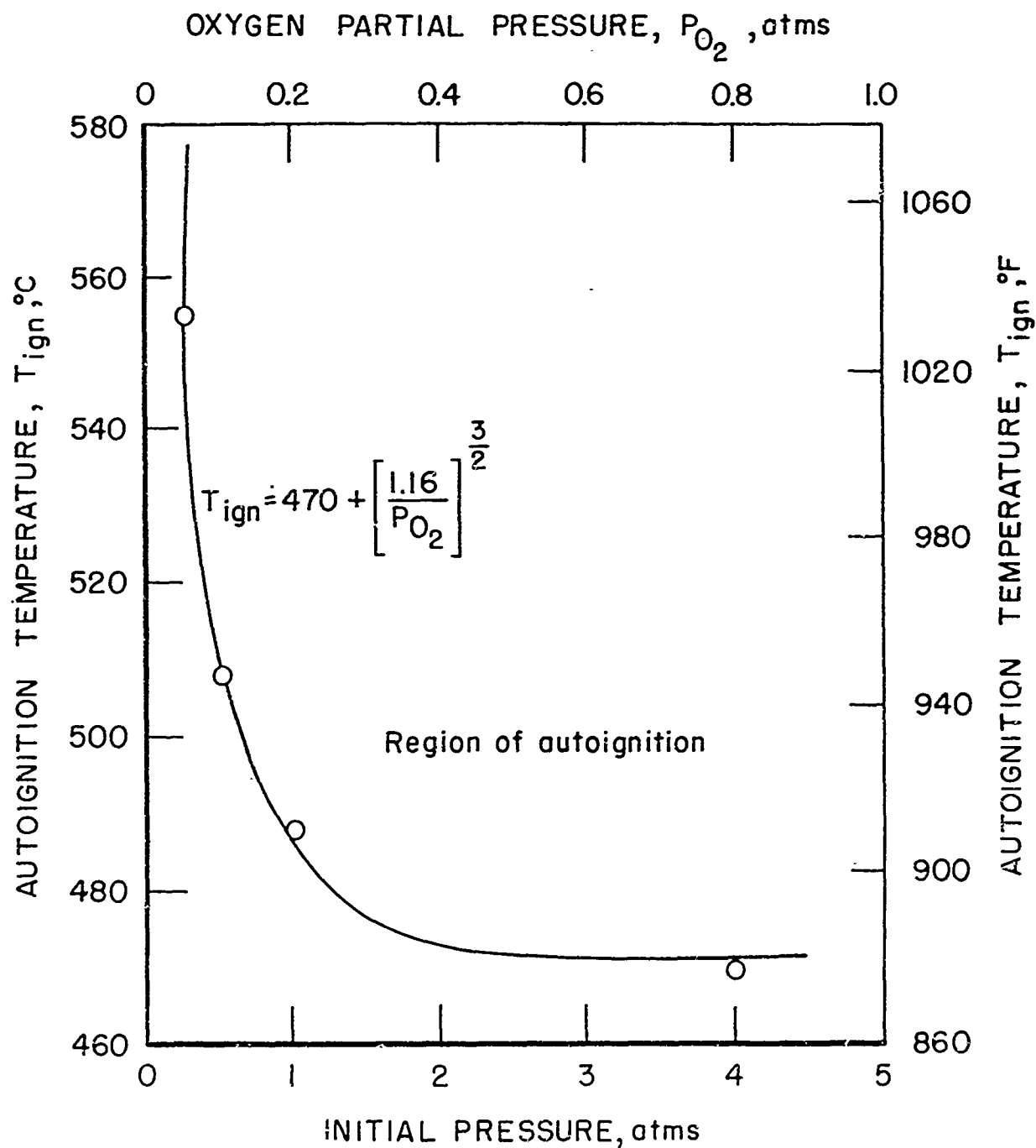


Figure 18. Minimum autoignition temperature of aromatic ether engine lubricant (Monsanto MCS-293) in air at various initial pressures and corresponding oxygen partial pressures (2540 cc stainless steel vessel).

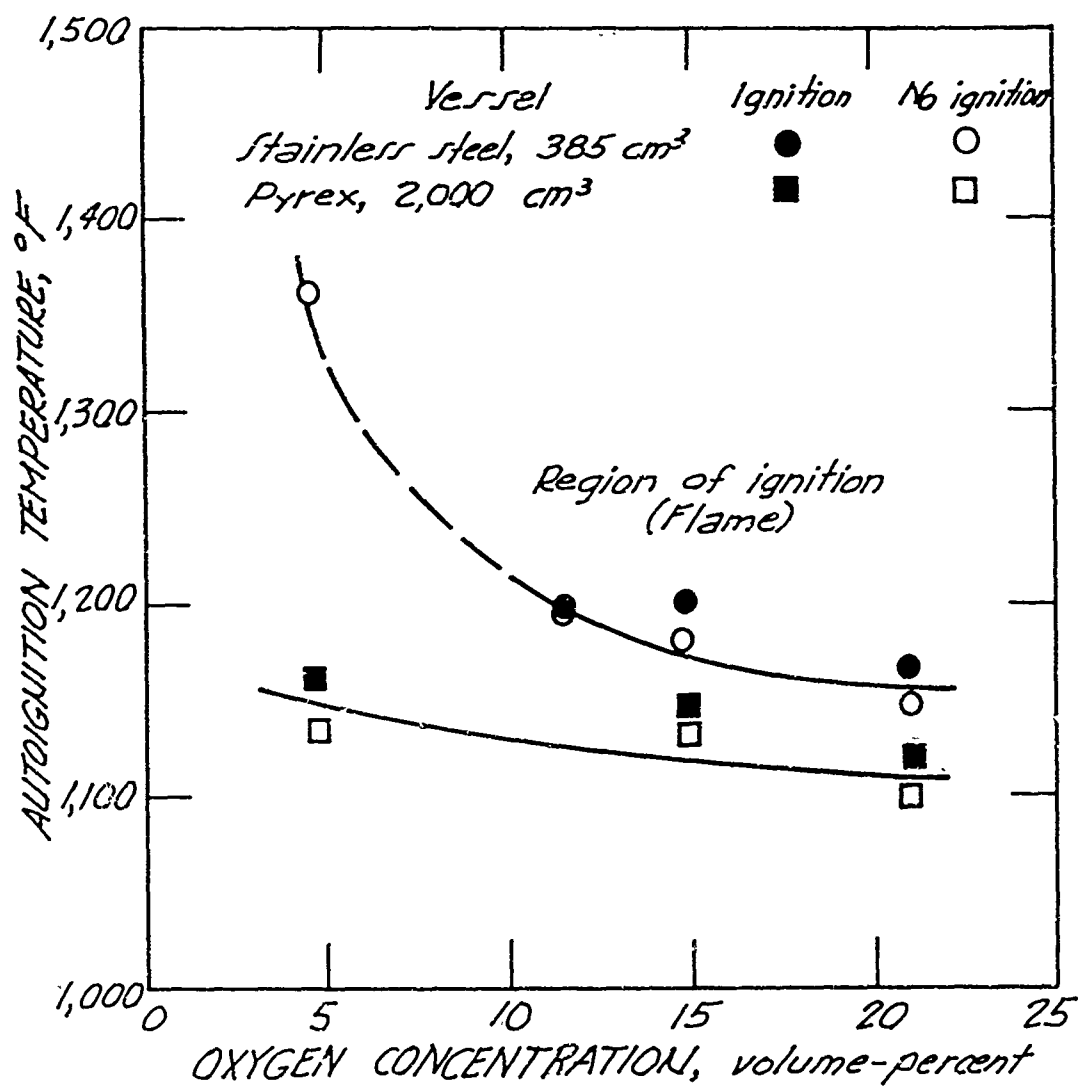


Figure 19. Minimum autoignition temperature of jet lubricant OS-124 in various oxygen-nitrogen atmospheres at one atmosphere pressure.

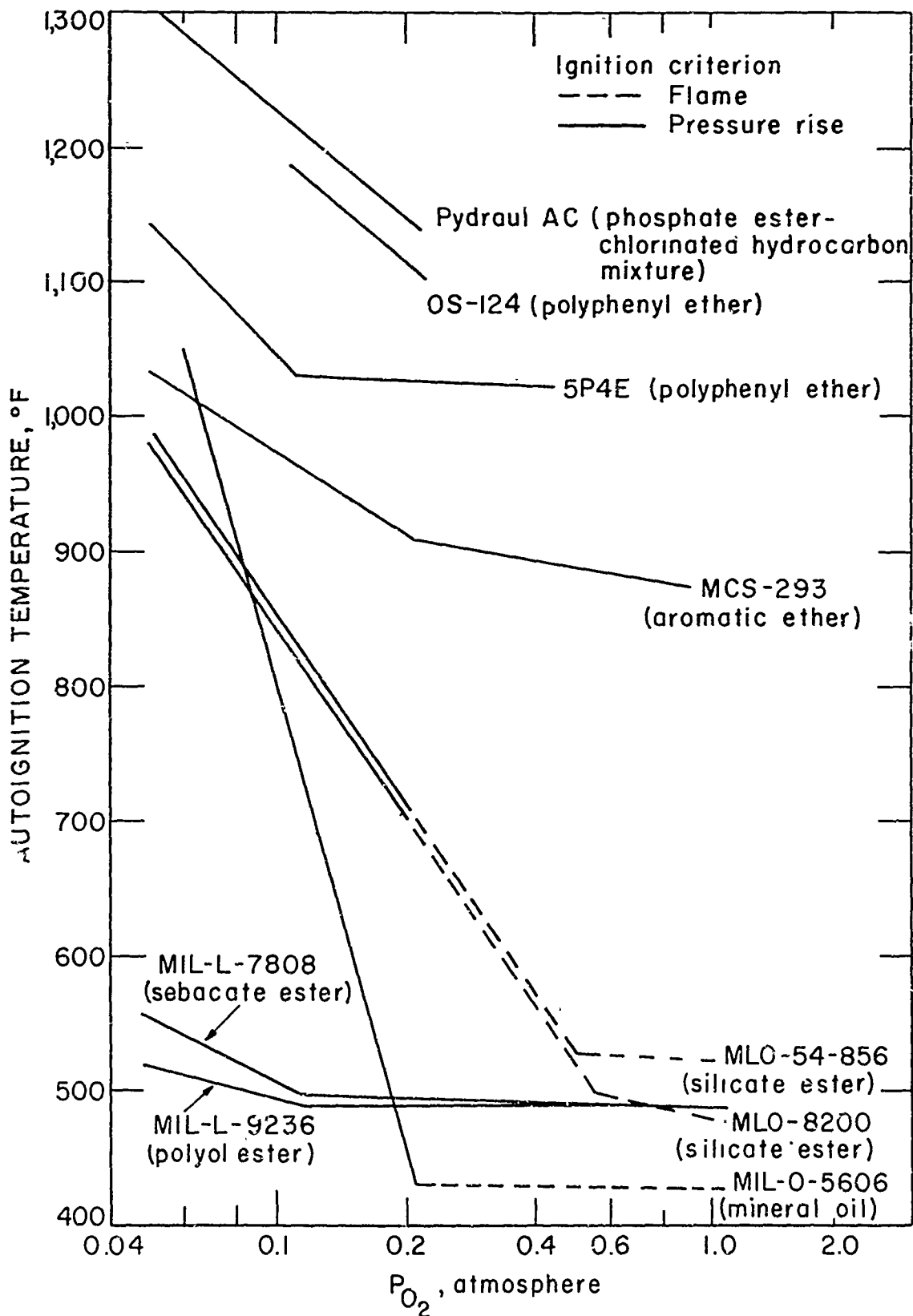


Figure 20. Variation of minimum autoignition temperature with oxygen partial pressure (P_{O_2}) for various lubricants.

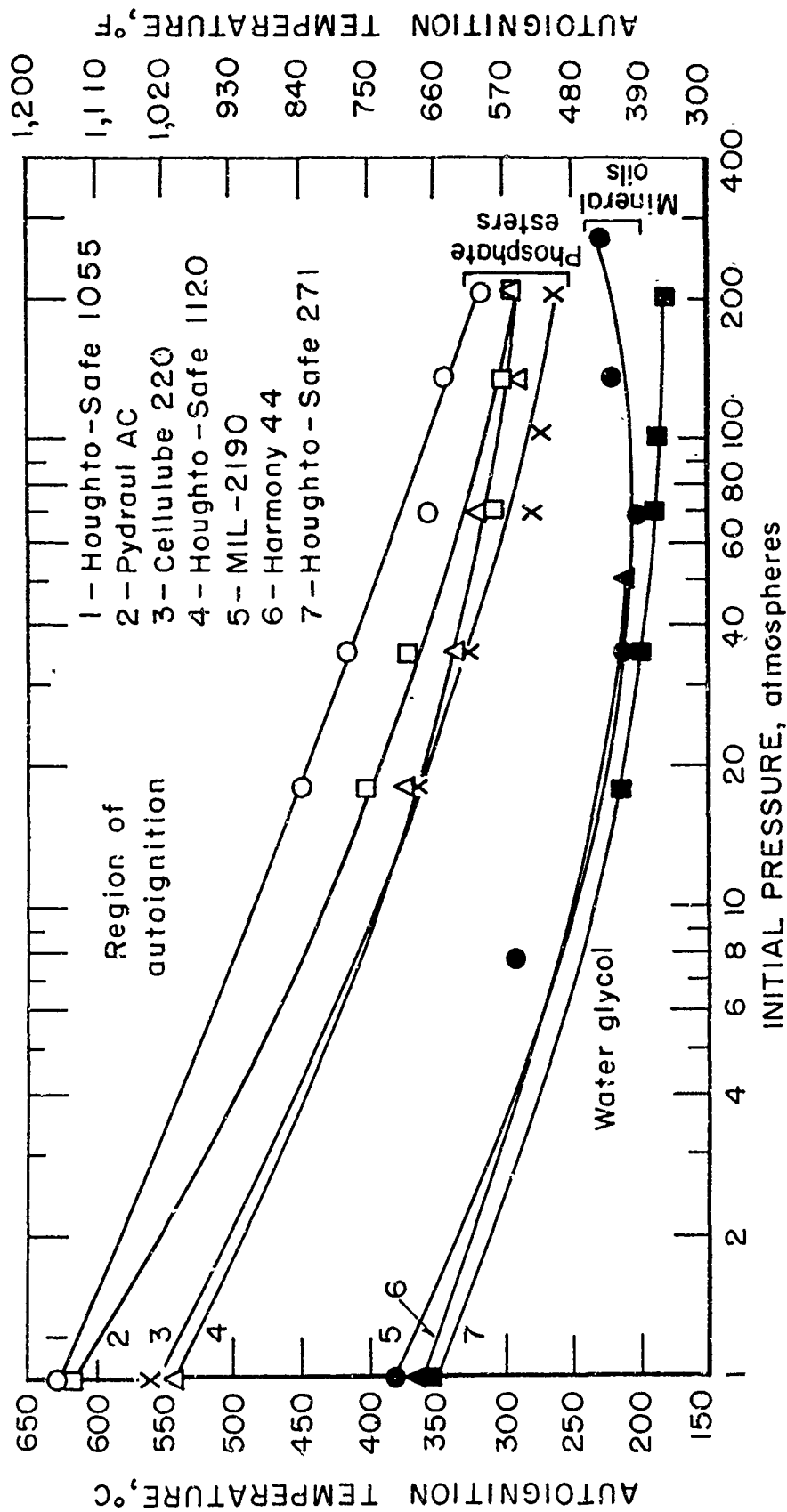


Figure 21. Variation in minimum autoignition temperature with pressure of commercial phosphate ester, mineral oil, and water-glycol lubricants in air. (200 cc glass vessel at 1 atmosphere and 450 cc steel vessel at elevated pressures).

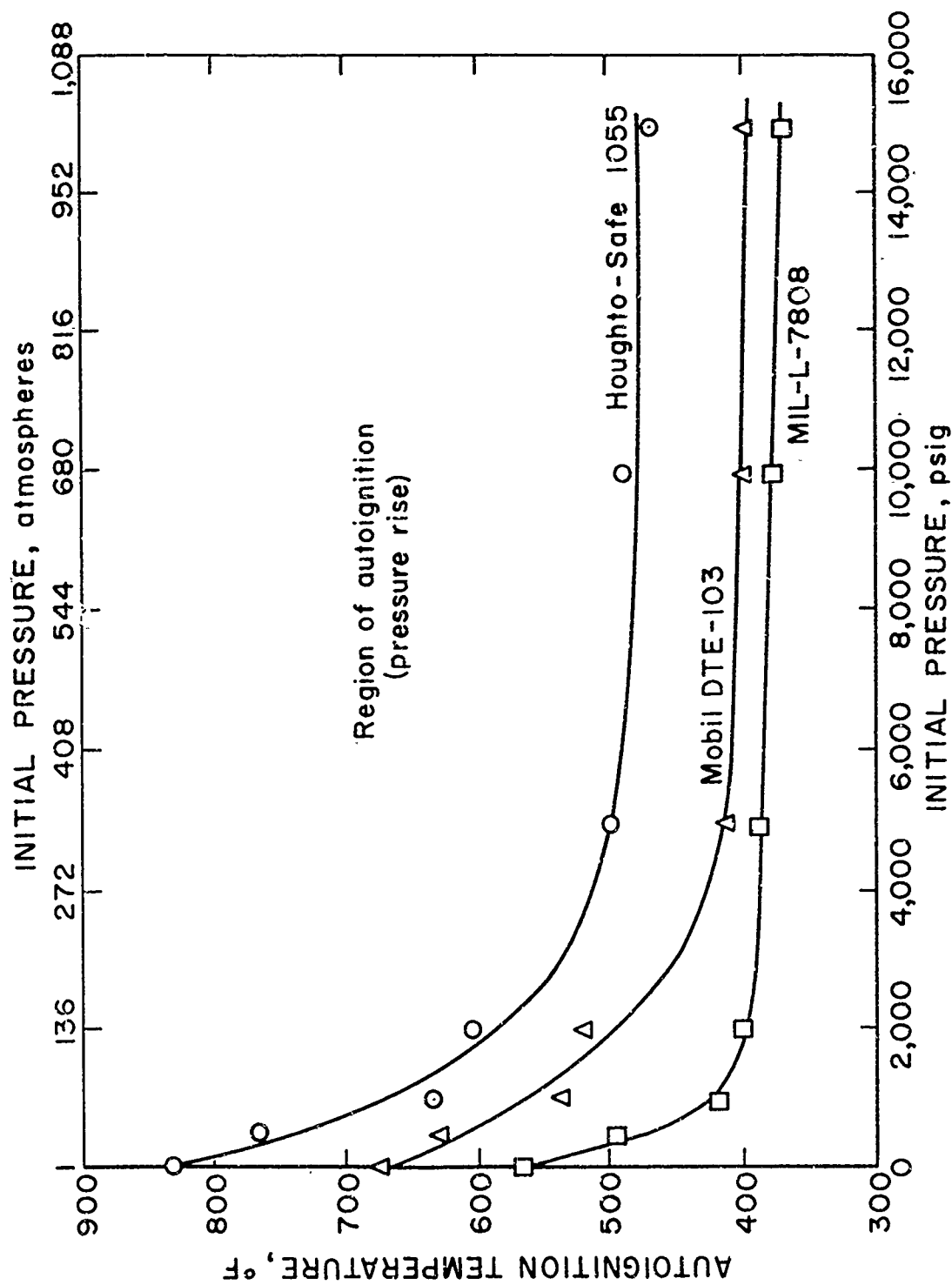


Figure 22. Minimum autoignition temperatures of Houghto-Safe 1055, Mobil DTE 103, and MIL-L-7808 lubricants in air at various initial pressures (275 and 46 cc steel vessels).

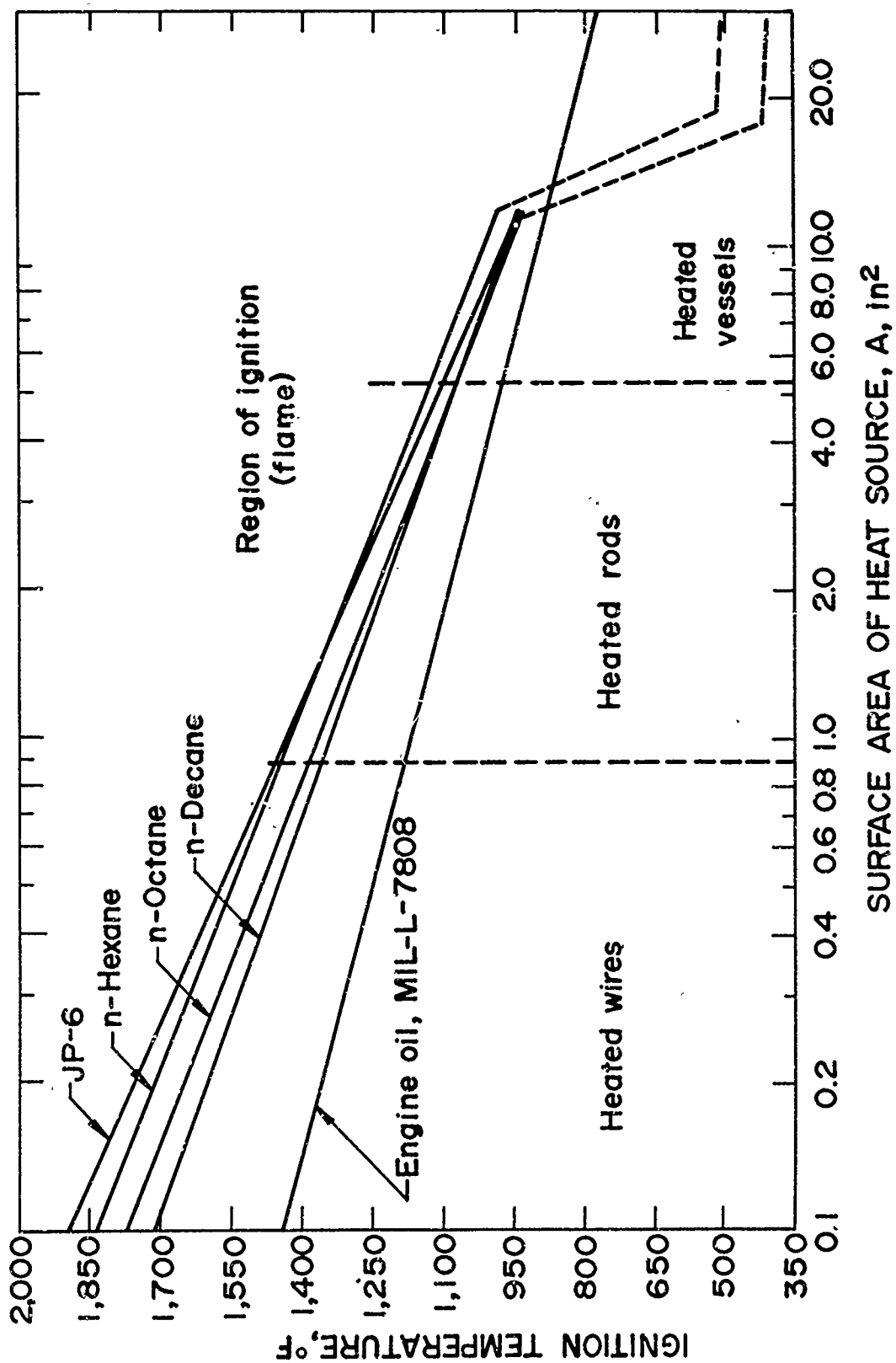


Figure 23. Hot surface ignition temperature as a function of the surface area of the heat source for various hydrocarbon fuels and an engine oil in air.

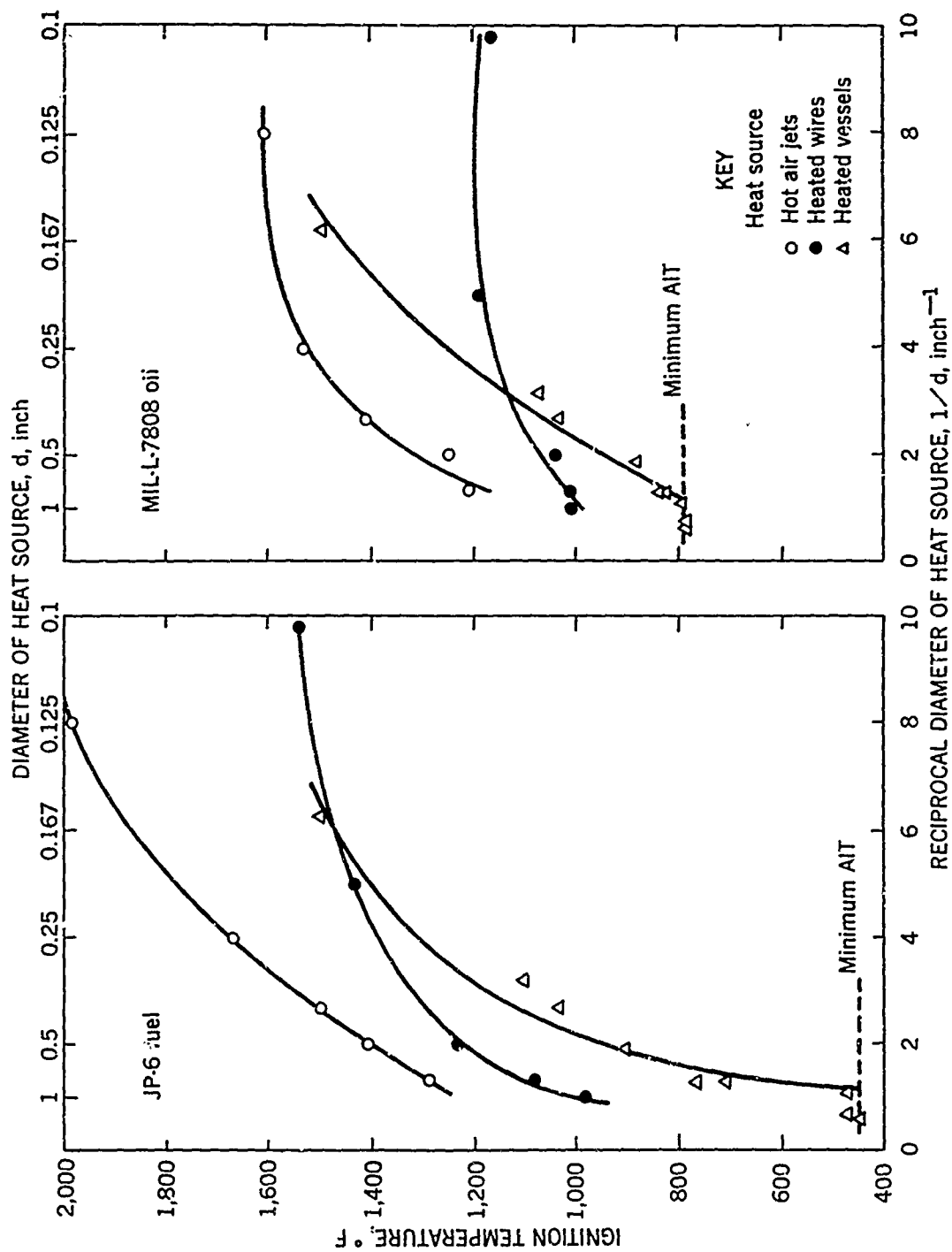


Figure 24. Variation of hot gas and hot surface ignition temperatures with reciprocal diameter of heat source for JP-6 fuel and MIL-L-7808 engine oil vapor-air mixtures.

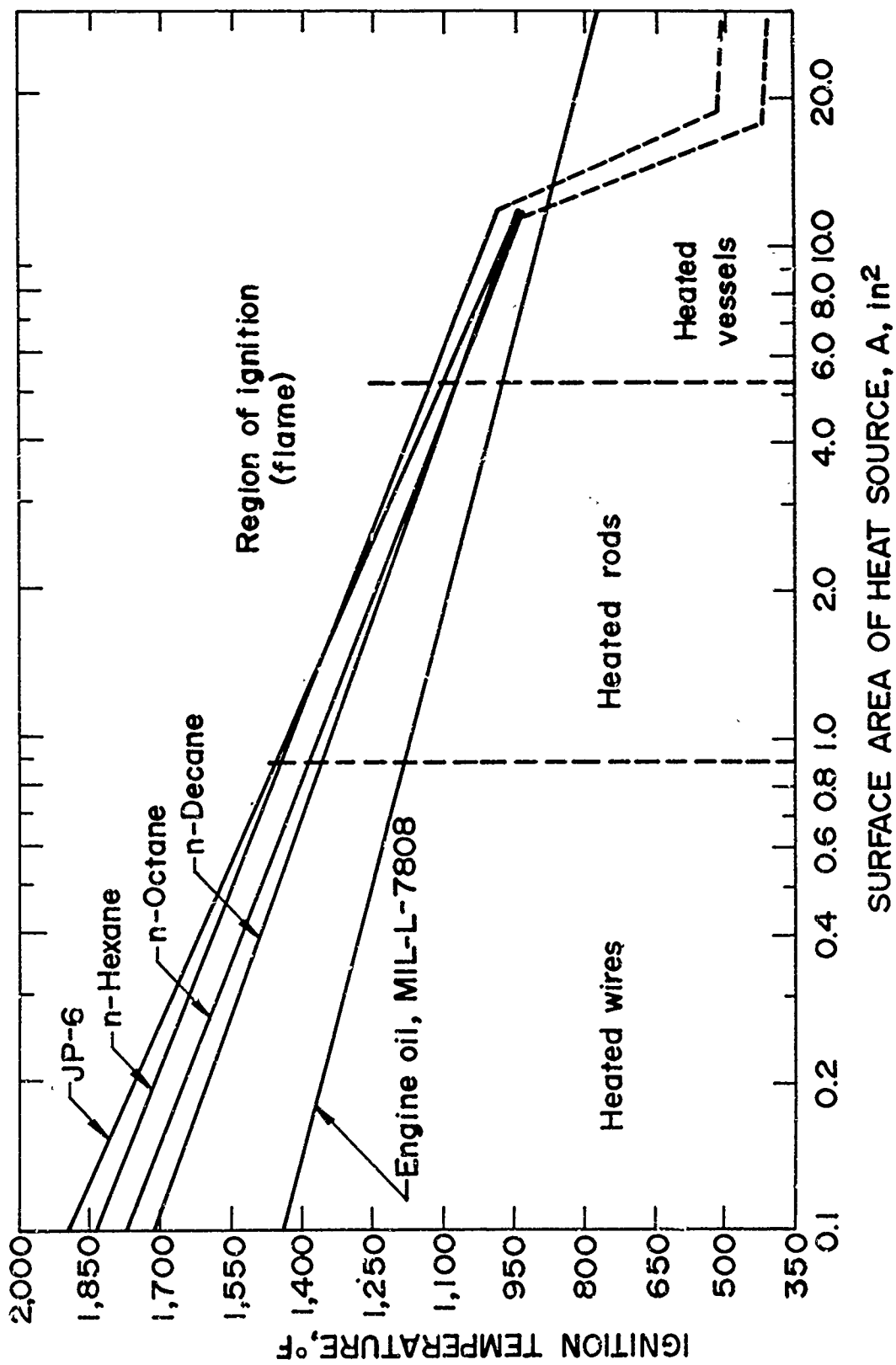


Figure 23. Hot surface ignition temperature as a function of the surface area of the heat source for various hydrocarbon fuels and an engine oil in air.

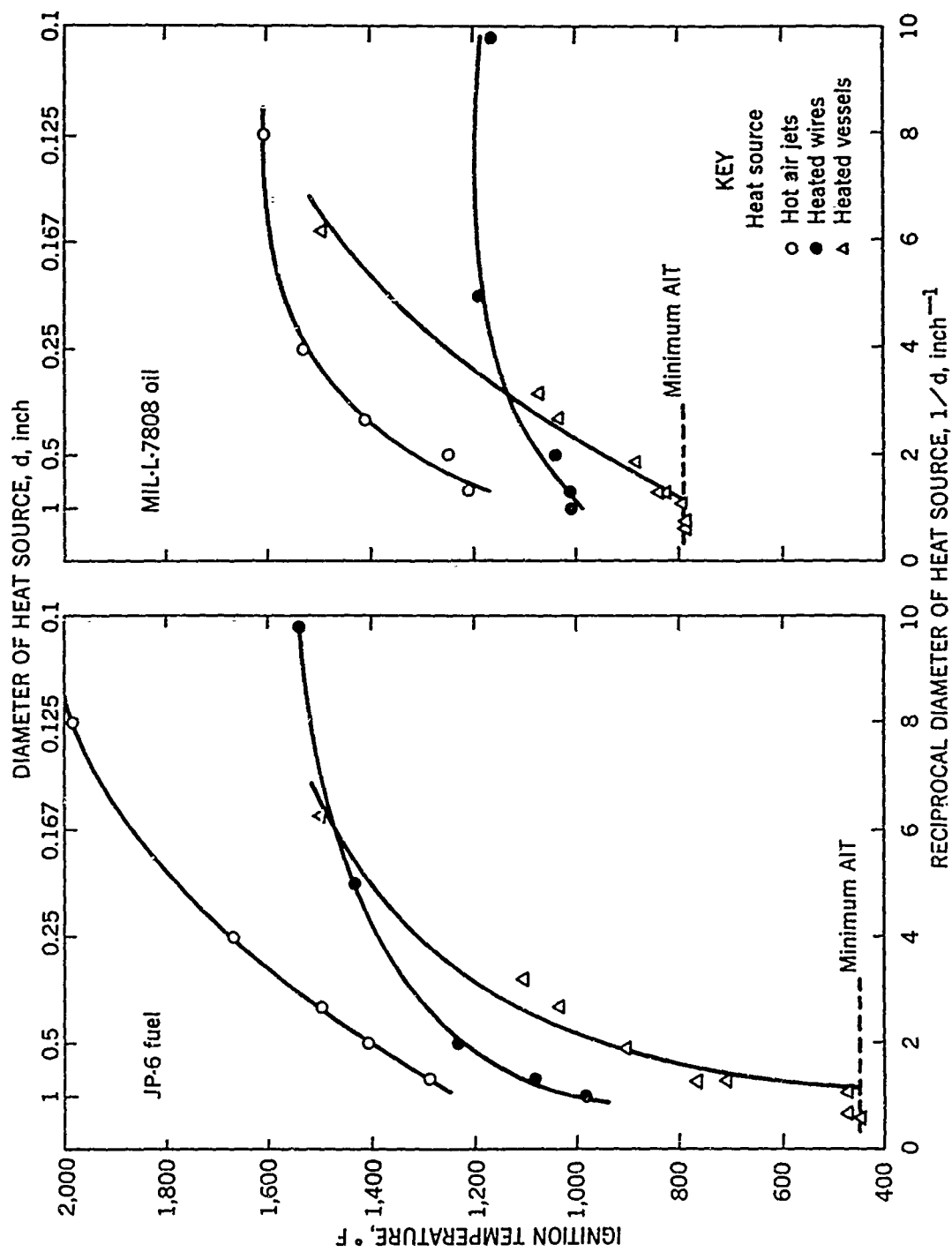


Figure 24. Variation of hot gas and hot surface ignition temperatures with reciprocal diameter of heat source for JP-6 fuel and MIL-L-7808 engine oil vapor-air mixtures.

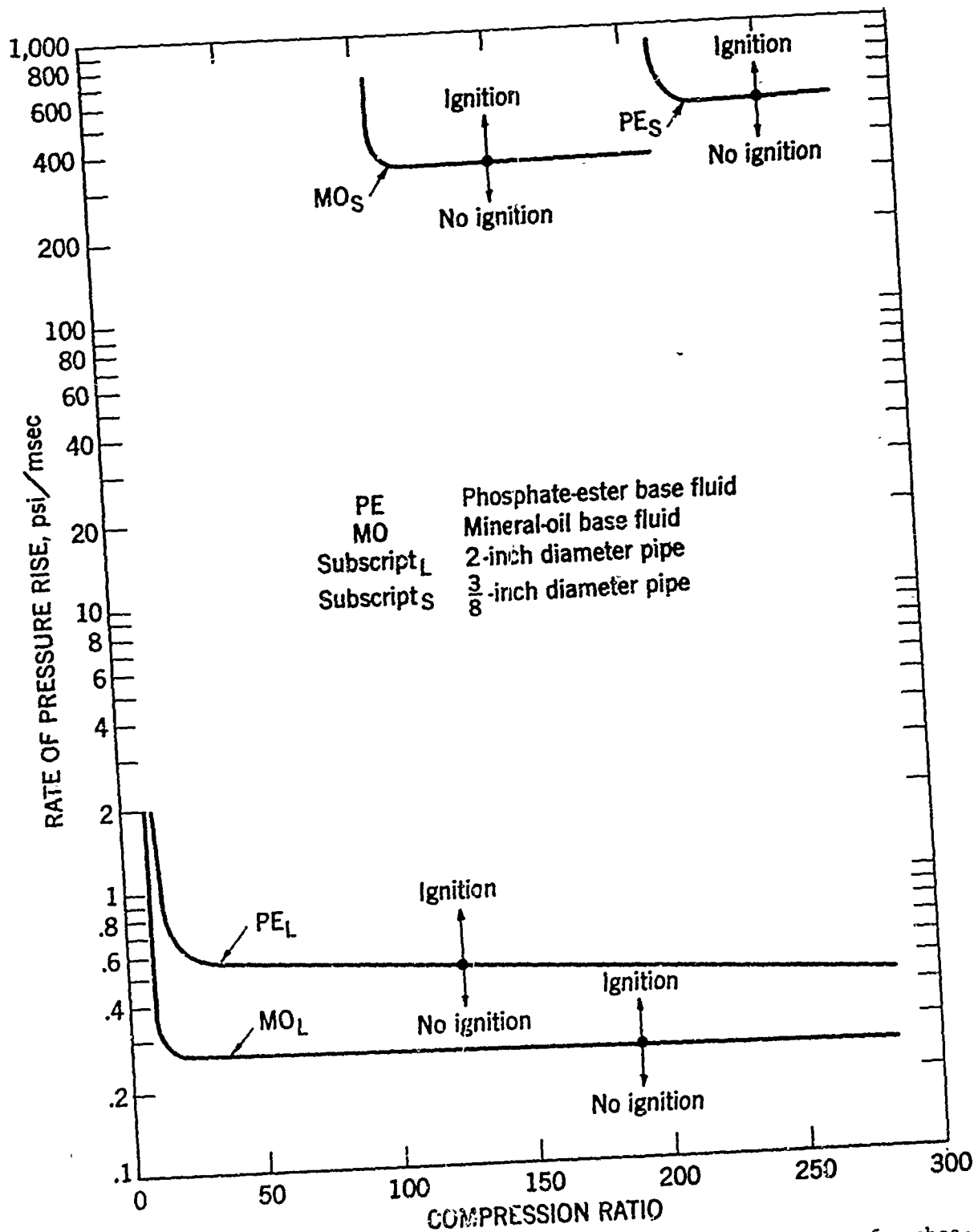


Figure 25. Rate of pressure rise required for compression ignition of a phosphate-ester base lubricant (Cellulube 220) and a mineral-oil base lubricant (MIL-2190 TEP) as a function of compression ratio in 3/8-inch and 2-inch diameter pipes.

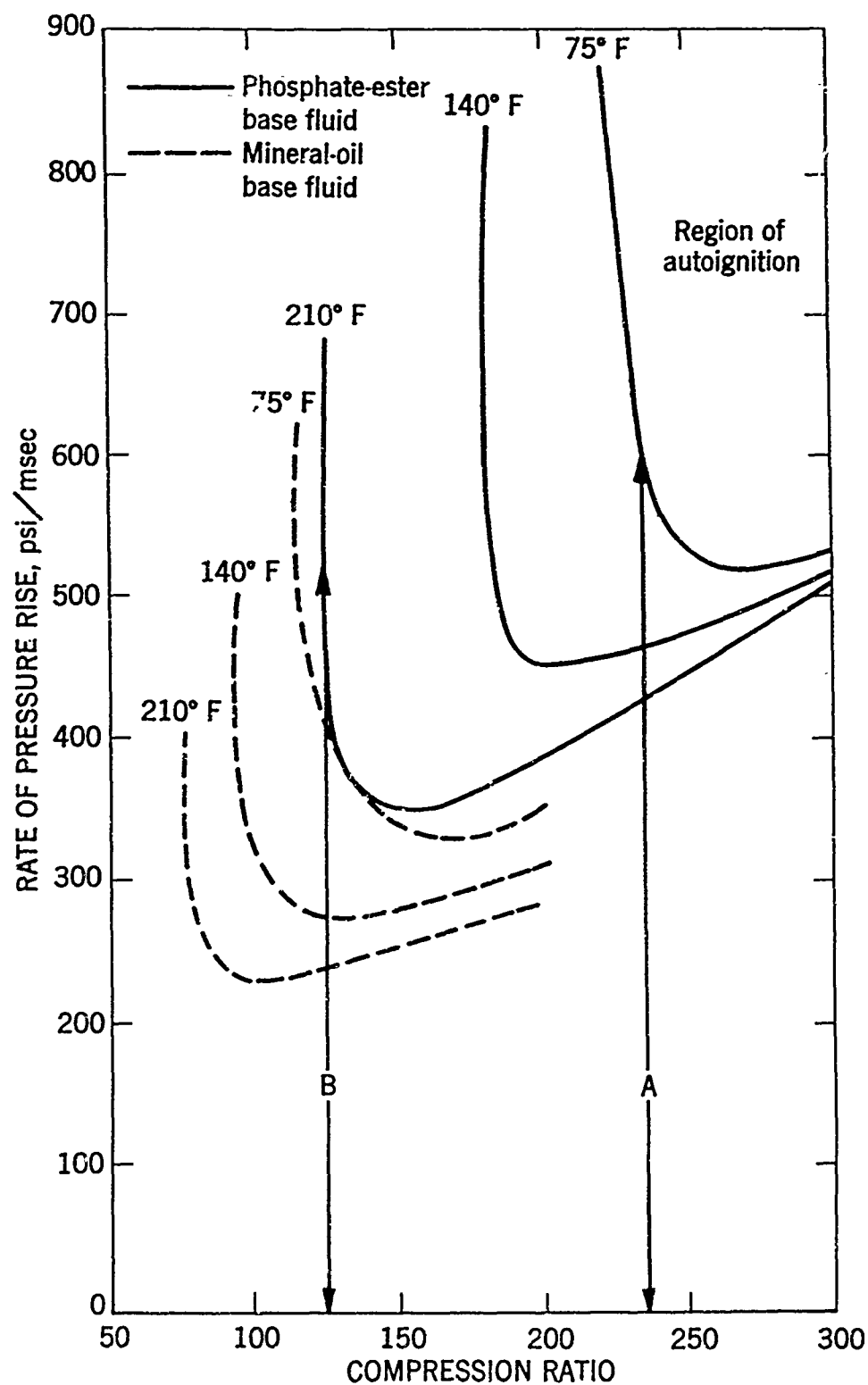


Figure 26. Rate of pressure rise required for ignition of a phosphate-ester base lubricant (Cellulube 220) and a mineral-oil base lubricant (MIL-290 TEP) as a function of compression ratio at various temperatures in a 1-foot length of 3/8-inch diameter pipe.